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PHYSICAL REVIEW.

THE MAGNETIC SUSCEPTIBILITY OF WATER.

BY HERMAN D. STEARNS.

THE magnetic susceptibility of water at a given temperature, such as 20° C., is regarded as one of the constants of nature, but there is no general agreement as to its numerical value. Table I. contains the results published by a number of careful observers. In writing the susceptibility (K) no correction has been made for the susceptibility of air. The temperature coefficient of (K) is of the order of .002, hence reduction to a common temperature could not bring the results into agreement.

TABLE I.

Determinations of (K).

Date.	Observer.	Temperature.	K 10^6.
1885	Quincke [1]	20° C.	−.84
1888	DuBois [1]	15	−.86
1892	Henrichsen [2]		−.75
1895	Curie [3]	18	−.79
1896	Townsend [4]	10	−.77
1898 } 1901 }	Königsberger [5]	22	−.80
1899	Jäger and Meyer [6]	18	−.66

[1] Wied. Ann., Vol. 35, p. 137, 1888.
[2] Wied. Ann., Vol. 45, p. 38, 1892.
[3] Journal de Physique, p. 206, 1895.
[4] Proc. Roy. Soc. London, 60, p. 186, 1896–7.
[5] Wied. Ann., Vol. 66, p. 698, 1898; Drude's Ann., Vol. 6, p. 506, 1901.
[6] Wied. Ann., Vol. 67, p. 712, 1899; Drude's Ann., Vol. 6, p. 870, 1901.

With the assistance of Mr. Angus L. Cavanagh, a student of physics in Stanford University, I have made a new determination.

We have used that general method in which a right cylinder of water of cross-section (q) is set perpendicular to a magnetic field whose strength at one end of the cylinder is equal to (H) and at the other end is negligible. (K) is given by the equation,

$$K = -\frac{2gp}{H^2q},$$

where (p) is the numerical value of the magnetic repulsion in grams on the cylinder in the direction of its axis. The value of (g) in this locality is 980.

In determining (p) we used a balance as Jäger [1] and Meyer did in their third determination. A glass tube was suspended from one end of a non-magnetic balance. The lower end was sealed abruptly and reached the center of the air space between the parallel pole-pieces of a large electromagnet. In this position the change in the weight of the tube due to exciting the magnet was determined by several successive weighings. The tube was then filled with water to a height at which the field strength was negligible and the weighings were repeated. Table II. contains the record of the weighings and the computed value of (p) for the four different tubes that were used. The changes of weight indicated by (p') and (p'') in Table II. were made by the use of a single rider whose mass was determined by each of us separately by comparison with a standard mass. Our results differed by .05 per cent.

The cross-section (q) of the cylinder of water contained in each tube was determined by the usual method of calibrating tubes by means of mercury. The height of the mercury column was read by each of two micrometer microscopes furnished by the Geneva Society, one of them belonging to the "comparateur" furnished by this society. The mercury was weighed on an ordinary analytical balance. Explorations of the magnetic field showed that the cross-section (q) should be measured between the heights of 1.5 cm. and 4.5 cm. above the lower end of the tube. Above 4.5 cm. the field strength was so small relatively that slight variations in (q) could

[1] Wied. Ann., vol. 67, p. 707, 1899.

produce no appreciable effect, and below 1.5 cm. no lack of uniformity in the field was found. The values found for (q) are given in Table II.

The water used was distilled from rain water caught in a glass vessel as it fell from a tile roof after copious showers had cleaned the roof. The water was condensed in tubes Nos. 1, 2 and 3 directly from the still. That in tube No. 4 had been in another glass vessel for some months. Experiment showed, however, that even water from the University water system gave the same values for (K) as the nearly pure water used.

TABLE II.

Values of (p), (q) *and* $\left(\frac{p}{q}\right)$.

Temperature.	Current of Electromagnet.	Repulsion.
Tube No. 1. (q) = 1.282 sq. cm.		
Tube empty.		
(t)	(c)	(p')
21	12	−.0039
23	12	−.0038
23	12	−.0038
24	12	−.0039
24	12	−.0038
24	12	−.00385
22	12	−.0039
24	12	−.0039
Mean 23	12	−.00385
Tube filled with water.		
(t)	(c)	(p'')
22	12	.0290
22	12	.0290
22	12	.0290
24	12	.0291
Mean 23	12	.02902
Water alone (calculated).		
(t)	(c)	(p) = (p'' − p')
23	12	.03287

TABLE II.—*Continued.*

Tube No. 2. $(q) = 1.279$.

Tube empty.

	(t)	(c)	(β')
	25	12	−.0038
	22	12	−.0039
Mean	23	12	−.00385

Tube filled with water.

	(t)	(c)	(β'')
	24	12	.0291
	22	12	.0291
	22	12	.0290
	20	12	.0290
Mean	22	12	.02905

Water alone (calculated).

(t)	(c)	$(\beta) = (\beta'' - \beta')$
23	12	.0329

Tube No. 3 $(q) = 1.333$.

Tube empty.

	(t)	(c)	(β')
	25	12	−.0068
		12	−.0066
Mean	25	12	−.0067

Tube filled with water.

	(t)	(c)	(β'')
	23	12	.0275
	23	12	.0275
	23	12	.0274
Mean	23	12	.02747

Water alone (calculated).

(t)	(c)	$(\beta) = (\beta'' - \beta')$
23	12	.03417

TABLE II.—*Continued.*

Tube No. 4. $(q) = .469$.

Tube empty.

	(t)	(c)	(p')
	21	11.7	−.0011
	21	11.6	−.0012
	24	11.3	−.00115
	22	12	−.0012
Mean	22	11.7	−.00116

Tube filled with water.

	(t)	(c)	(p'')
	20	12	.0109
	20	12	.0109
	22	11.6	.0108
Mean	21	11.9	.01087

Water alone (calculated).

(t)	(c)	$(p) = (p'' - p')$
21	12	.01205

Values of (p/q).

No. of Tube.	Temperature.	(p/q)
1	23	256.4
2	23	257.2
3	23	256.3
4	21	256.9
Mean	23	256.7

The close agreement of the values of (p/q) would seem to show that the mean value cannot be in error by more than .5 per cent.

In determining the field strength (H) three test coils were used. Coil No. 1 was mounted so that it could be turned through 180° in the field (H). Coils No. 2 and 3 were mounted on handles so that they could be drawn out of the same field. No. 2 and No. 3 were of nearly the same diameter and were wound with nine turns of wire each. Coil No. 1 was of smaller diameter and was wound with six turns of wire. Its effective area was almost exactly the same as that of the other two, its actual area being doubled on account of its turning through 180°. An astatic mirror galvanom-

eter of long period placed at a sufficient distance from the electromagnet was connected in series with the three coils, and the galvanometer deflections due to operating in the field (H) with the coils were observed. After continued practice a comparison of the three coils was made and the results are given in Table III.

TABLE III.

Comparison of the test coils in the field (H).

No. of Coil.	Area (A).	Deflection (a).	Current.	a/A
3	16.84	212	11.8	1.259
1	16.92	213	11.8	1.259
2	16.88	212	11.7	1.256
3		212	11.7	
1		213	11.7	
2		212	11.7	
3		212	11.7	
1		213	11.7	
2		212	11.7	

This agreement being satisfactory coils No. 1 and No. 3 were selected for further use.

As a standard instrument a current inductor of the pattern described on page 224 of Henderson's Practical Electricity and Magnetism was used. The formula for the number of lines of force cut by the test coil of such a current inductor when the current through its solenoid is broken is

$$N_1 = \frac{4\pi n n_1 CA}{10}\left(1 - \tfrac{1}{2}\frac{r^2}{l^2}\right).$$

Measurements of the constants of this instrument gave, for the value of (N_1),

$$N_1 = 210 \cdot 10^3 C.$$

(C) was measured by Weston direct-reading portable ammeter No. 10364 whose indications are certified to by the company as correct to .25 per cent.

To test the accuracy of the measured constant of the current inductor, this inductor was connected in series with an earth induc-

tor and the galvanometer, and the deflections of the two inductors were compared. The result is given in Table IV.

TABLE IV.

Comparison of earth inductor and current inductor.

Inductor Operated.	Deflection.	Current in Solenoid of Current Inductor.
Current	237	.717
Earth	235	
Current	236.5	.715
Earth	234.5	
Current	234	.710
Earth	234.5	
Current	234.5	.712
Earth	235	
Current	234.5	.712
Earth	235	
Mean { Current	235.3	.713
Mean { Earth	234.8	
Calculated { Current	234.8	.712
Calculated { Earth	234.8	

The formula for the earth indicator is

$$N_2 = 2A'H',$$

where (H') is the horizontal component of the earth's magnetic field.

The mean of four determinations of (H') by means of a Kew magnetometer set up where the earth inductor was used gave

$$(H') = .2482.$$

Hence

$$N_2 = 2.301 \cdot 10^3 \cdot .248 = 149300.$$

For N', using for (C) the value .712 taken from Table IV., we have

$$N' = 210 \cdot 10^3 \cdot .712 = 149500.$$

This good agreement seemed to justify the use of the current inductor as an absolute standard.

To determine (H) by comparison with the field of the current inductor, coil No. 1 was connected in series with the test coil of the inductor and with the galvanometer, and the deflections due to rotating coil No. 1 in the field (H) and to breaking the current through the solenoid of the current inductor were observed. Coil No. 1 was then replaced by coil No. 3 and two more series were made on different days. The results are given in Table V.

TABLE V.

Value of (H).

	Instrument Operated.	Deflection.	Current in Solenoid.	Current in Electromagnet.
		First series.		
	Current inductor.	233	.669	
	Coil No. 1.	233		12
	Current inductor.	233	.668	
	Coil No. 1.	234		12
	Current inductor.	234	.670	
	Coil No. 1.	233		12
	Current inductor.	234	.670	
	Coil No. 1.	234		12
Mean	Current inductor.	233.5	.669	
	Coil No. 1.	233.5		12
		Area of coil No. 1, 16.92.		
		$H = \frac{210 \cdot 10^3 \cdot .669}{16.92} = 8300.$		
		Second series.		
	Current inductor.	222	.666	
		220	.666	
		220	.664	
		220	.663	
		219	.663	
	Coil No. 3.	219		11.7
		219		11.7
Mean	Current inductor.	220	.665	
	Coil No. 3.	219		11.7
Calculated	Current inductor.	220	.665	
		220		12

TABLE V.—*Continued.*

Third series.

	Current inductor.	222	.678	
		220	.668	
		220	.668	
		223	.679	
	Coil No. 3.	220		12
	Current inductor.	219	.666	
	Coil No. 3	219		12
	Current inductor.	219	.665	
	Coil No. 3.	219		12
Mean	Current inductor.	220.5	.6706	
	Coil No. 3.	219.3		12
Calculated	Current inductor.	219.3	.667	
	Coil No. 3.	219.3		12

Mean current in solenoid in second and third series .666
Area of coil No. 3 16.84

$$H = \frac{210 \cdot 10^3 \cdot .666}{16.84} = 8300.$$

In view of the agreement between the current inductor and the earth inductor and also among the test coils, a greater error than 1 per cent. in the value of (H) seems very improbable.

Careful explorations of the magnetic field showed that the residual field and the field at the top of the water cylinder were negligible. Hence it is correct to use as the formula for (K)

$$K = -\frac{2gp}{H^2 q}.$$

The first four lines of Table VI. contain the values for K calculated from the values of (p/q) in Table II. and from the value of (H) in Table V.

The poles of the electromagnet were moved closer together and another determination of (K) was made by the same method and with the same apparatus. This value appears in the fifth line of Table VI.

The poles were brought back to their original position and additional determinations were made, the field strength being varied

by changes in the exciting current of the electromagnet. The results are given in the last three lines of Table VI.

TABLE VI.

Values of (K).

Temperature.	(H)	$(K \cdot 10^6)$
23	8300	−.730
23	8300	−.732
23	8300	−.730
21	8300	−.731
22	9700	−.734
22	8150	−.736
22	8030	−.735
21	7470	−.738
Mean 22		−.733

Admitting a possible error of 1 per cent. in the measurements of (H) and of .5 per cent. in the measurements of $\left(\frac{p}{q}\right)$ the maximum possible error in the result would be 2.5 per cent., and it would seem certain that the true value of (K) lies between the values $-.715 \cdot 10^{-6}$ and $-.750 \cdot 10^{-6}$ at the temperature of 22° C.

Opposed to this conclusion stand the results of all the observers quoted in Table I. except that of Henrichsen. The situation is well expressed by Jäger and Meyer,[1] who say, " Eine ausreichende Erklärung für die starken Abweichungen der Resultate der verschiedenen Beobachter steht sonach noch aus."

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STANFORD UNIVERSITY, CAL., September, 1902.

[1] Drude's Ann., Vol. 6, p. 870, 1901

THERMODYNAMIC FORMULÆ FOR ISOTROPIC SOLIDS SUBJECT TO TENSION IN ONE DIRECTION.

By J. R. Benton.

THE purposes of this note are (1) to establish some thermodynamic formulæ for isotropic solids, when acted upon by no external forces except a uniformly distributed tension in one direction; and (2) to show that in consequence of these formulæ the coefficient of expansion and the specific heat of most isotropic substances must increase with increasing tension, the change in specific heat being however very small.

Consider a wire or rod of uniform cross section, subjected to tension. Let us exclude all actions upon it from outside, except the following: (1) the tension may be changed (inside the elastic limit); and (2) heat may be added (or abstracted). Let us assume that no internal changes take place in the wire, except as accompanying one of the above-named actions from outside; and that then the internal change is determined by the action from outside. This assumption can be realized by metal wires. Under these limitations the system will have but two degrees of freedom.

Let us assume further that the wire has been reduced to the "normal elastic state" by repeated heating and cooling under varying tension; the effects of elastic hysteresis can then be neglected. When all these conditions are fulfilled, experiments show (1) that all processes which our assumptions admit, are reversible, or at least can be made as nearly so as we please, by making them proceed sufficiently slowly; and (2) that the state of the system can be completely defined by two independent variables. These variables may be chosen in various ways; we shall find it most convenient to use the absolute temperature (T) in centigrade degrees, and the tension (P) in dynes per square centimeter.

Suppose T and P to increase; we know from experiment that the corresponding increase in the length l is given by

$$dl = l_0(adT + bdP), \tag{1}$$

where l_0 is the length at 0° C. and no tension, a is the coefficient of linear thermal expansion, and b is the reciprocal of Young's modulus. a and b are not constant, but are to be considered as functions of T and P.[1]

If heat is added to the wire, we have

$$dQ = M(c_P dT + \beta dP), \tag{2}$$

where Q is the quantity of heat in gram calories, M is the mass of the wire, c_P the specific heat at constant tension, and β is a coefficient to which no name has been given, but which might be called the latent heat of change of tension. c_P and β are to be considered as functions of T and P.[1]

For the work W, in ergs, done upon the wire, we have

$$dW = qPdl = ql_0(PadT + PbdP), \tag{3}$$

where q is the cross-section. In this expression we neglect the very small amount of work done by (or against) atmospheric pressure as the wire contracts (or expands) laterally.

For the internal energy E, in ergs, we have, since mechanical work and heat are the only kinds of energy that enter or leave the system,

$$dE = dW + JdQ = (ql_0Pa + MJc_P)dT + (ql_0Pb + MJ\beta)dP, \tag{4}$$

where J is the mechanical equivalent of heat, in ergs per gram-calorie.

Since we consider only reversible processes, an infinitesimal change in the entropy (H) is given by the equation $dH = dQ/T$. We have accordingly

$$dH = \frac{Mc_P}{T}dT + \frac{M\beta}{T}dP. \tag{5}$$

[1] That is, as long as we work with the same wire. a and b may have different values for another wire of the same substance, under the same conditions as to temperature and tension.

Passing in review the quantities under our consideration, we may classify them into (1) known constants, l_0, q, M, and J; (2) quantities of independent physical significance, T, P, l, E, H, W and Q; and (3) coefficients — a, b, c_P, and β — defined in terms of the derivatives of the quantities of class (2). It is our problem to establish relations between these coefficients and their derivatives with respect to T and P.

Equations (1)–(5), involving the coefficients a, b, c_P, β, and the known constants, give the differentials of l, W, Q, E, H, in terms of the differentials of the independent variables T and P. dW and dQ are not perfect differentials; but we know by experiment that dl is a perfect differential, under the conditions we have assumed. dE and dH are perfect differentials, by the first and second fundamental principles of thermodynamics.

We have, then, from (1), (4) and (5)

$$\left(\frac{\partial b}{\partial T}\right)_P = \left(\frac{\partial a}{\partial P}\right)_T \tag{6}$$

$$\left(\frac{\partial [ql_0Pb + MJ\beta]}{\partial T}\right)_P = \left(\frac{\partial [ql_0Pa + MJc_P]}{\partial P}\right)_T \tag{7}$$

$$\left(\frac{\partial [M\beta/T]}{\partial T}\right)_P = \left(\frac{\partial [Mc_P/T]}{\partial P}\right)_T, \tag{8}$$

where $\left(\frac{\partial}{\partial T}\right)_P$ means the derivative with respect to T at constant tension, and $\left(\frac{\partial}{\partial P}\right)_T$ means the derivative with respect to P at constant temperature.

Carrying out the differentiations in (7) and (8), and bearing in mind the relation (6), we have

$$MJ\left(\frac{\partial \beta}{\partial T}\right)_P = ql_0a + MJ\left(\frac{\partial c_P}{\partial P}\right)_T \tag{9}$$

$$\left(\frac{\partial \beta}{\partial T}\right)_P - \frac{\beta}{T} = \left(\frac{\partial c_P}{\partial P}\right)_T \tag{10}$$

Substituting in (9) the value of $\left(\frac{\partial \beta}{\partial T}\right)_P$ from (10) we get

$$\beta = \frac{ql_0}{MJ} \cdot aT = \frac{1}{\rho_0 J} \cdot aT, \tag{11}$$

where ρ_0 is the density at 0°C. and no tension.

Remembering that b is the reciprocal of Young's modulus, we can put (6) in the form

$$\left(\frac{\partial Y}{\partial T}\right)_P = -Y^2\left(\frac{\partial a}{\partial P}\right)_T, \tag{12}$$

where Y is Young's modulus.

By substituting in (10) the value of β from (11) we obtain

$$\left(\frac{\partial a}{\partial T}\right)_P = \frac{\rho_0 J}{T}\left(\frac{\partial c_P}{\partial P}\right)_T. \tag{13}$$

The last three equations are the ones to which it is desired to call attention.

Equation (11) gives an expression for the latent heat of increase of tension in terms of the coefficient of linear expansion, the absolute temperature, the density (at 0° C. and no tension), and the mechanical equivalent of heat. If we substitute the value of β given by this equation, in (2), and set $dQ = 0$, we obtain

$$dT = -\frac{aT}{c_P \rho_0 J} \cdot dP, \tag{14}$$

the well-known equation for the change in temperature due to a sudden (adiabatic) change of tension; this equation was derived by Lord Kelvin, and was made the basis of a determination of the mechanical equivalent of heat by Edlund.[1]

Equation (12) gives a relation between Young's modulus, its derivative with respect to the temperature (at constant tension), and the derivative of the coefficient of thermal expansion with respect to

[1] E. Edlund: Quantitative Bestimmung der bei Volumveränderung der Metalle entstehenden Wärmephänomene und des mechanischen Wärmeäquivalents. Pogg. Ann., CXXVI., pp. 539-572, 1865.

the tension (at constant temperature). As a consequence of this equation we may say: *If for a given substance Young's modulus decreases with rising temperature, then the coefficient of thermal expansion increases with increasing tension.* Since it is the general rule that Young's modulus *does* decrease with rising temperature, we may accept it as a general rule that the coefficient of thermal expansion of solid bodies is greater when they are under tension than when free.

According to (12) the coefficient of expansion of a metal wire, when strained to its elastic limit, may differ by several per cent. from its value when the wire is under no tension. In copper at 0° C., for instance, the difference may amount to about 5 per cent.

An equation similar to (12) is given, as a result of slightly different reasoning, by Dahlander,[1] who made experiments with copper, brass, german silver, iron and steel, to obtain the dependence of the coefficient of expansion on tension, and found a rough agreement with the formula. Dahlander determined the coefficient of expansion under different tensions; unfortunately he did not measure Young's modulus and its derivative with respect to the temperature for the *same* wires, but substituted in the formula the values obtained by other observers, with different wires. Accordingly no very close agreement with the formula can be expected, in view of the variation of mechanical properties in different specimens of the same substance.

Equation (13) gives a relation between the derivative of the coefficient of expansion with respect to the temperature, the derivative of the specific heat with respect to the tension, and the absolute temperature; the density and the mechanical equivalent of heat being supposed known quantities. As a consequence of this equation we may say: *If for a given substance the coefficient of expansion increases with rising temperature, then the specific heat (at constant tension) increases with increasing tension.* Since it is the general rule that the coefficient of expansion *does* increase with rising temperature, we may take it as a general rule that the specific heat of solid bodies increases as the tension is made greater.

[1] G. R. Dahlander: Versuch, den Ausdehnungskoeffizienten von Metalldrähten bei ungleichen Spannungsgraden zu bestimmen. Pogg. Ann., CXLV., pp. 147–153, 1872.

For most metals, however, this change in specific heat with the tension is inappreciable. Copper, for example, at 0° C., gives

$$\left(\frac{\partial c_P}{\partial P}\right)_T = \frac{T}{J\rho_0}\left(\frac{\partial a}{\partial T}\right)_P = \frac{273}{4.2 \times 10^7 \times 8.9} \times 4.04 \times 10^{-8} = 2.95 \times 10^{-14},$$

where P is expressed in dynes per square centimeter. Expressing P in kilograms weight per square millimeter, this becomes 2.89×10^{-6}. If the elastic limit is as high as 30 kilograms per square millimeter, the specific heat under this tension would differ by only 0.00009, or one tenth of one percent from its value under no tension. For steel, at 0° C., the tension would have to rise to 60 kilograms per square millimeter, before the specific heat would differ one fourth of one percent from its value under no tension. In these computations the values of $\left(\frac{\partial a}{\partial T}\right)_P$ given by Voigt [1] have been used. For other metals the results are of the same order of magnitude.

I am not aware that any attempt has ever been made to study the dependence of specific heat on tension experimentally.

The three equations (11), (12) and (13) were derived with T and P as independent variables. The normal variables of the system are l and T; T and P are inverse variables. By using the relation $dl = l_0 (adT + bdP)$, we could change the independent variables to l and T, or to l and P. Such transformations of course lead to no new *independent* relations, but may bring into prominence relations not otherwise apparent, or may reduce the equations to more convenient form. A thorough investigation of these transformations, however, has not led to expressions possessing either of these advantages. And the use of P as an independent variable, rather than l, has a great advantage, because P (and not l) is the quantity that can be varied directly (or kept constant) during experiments.

[1] W. Voigt : Wied. Ann.

ELASTICITY OF COPPER AND STEEL AT — 186° C.

By J. R. Benton.

KNOWLEDGE of the dependence of the elasticity of solids on temperature, aside from any scientific value in itself, is of interest also because inferences can be drawn from it regarding the variation of other mechanical and thermal properties,[1] and because of its possible bearing on the theory of intermolecular forces in solids.

The variation of elasticity with temperature has been studied by Wertheim,[2] Kohlrausch and Loomis,[3] Kupffer,[4] Streintz[5] and Kiewiet,[6] and was the subject of very careful researches by Pisati.[7] These investigators worked mostly above ordinary temperature; Wertheim extended his experiments to — 15° C.; the others did not go below 0°. The extremely thorough experiments of Pisati, which furnish such complete and accurate information[8] for the substances and temperatures he used, were made between 20° and 300° C.

[1] See article: Thermodynamic Formulæ for Isotropic Solids subject to Tension in one Direction, Phys. Rev.

[2] G. Wertheim: Untersuchungen über die Elastizität. Pogg. Ann., Ergänzungsband II., pp. 1–115, 1848.

[3] F. Kohlrausch and Loomis: Pogg Ann., CXLI., p. 481, 1870.

[4] A. Kupffer: Mém. de l'Acad. imp. de St. Petersbourg (VI. sér.), Vol. VI, p. 393, 1857.

[5] H. Streintz: Über die Änderung der Elastizität und der Länge eines vom galvanischen Strome durchflossenen Drahtes. Pogg. Ann., CL., p. 368, 1873.

[6] J. Kiewiet: Wiedermann's Ann., XXIX., 617–654, 1886.

[7] G. Pisati: Sulla Elasticità dei Metalli a diverse Temperature. Nuovo Cimento, 3d ser., Vol. I., p. 181; Vol. II., p. 137, 1877; Vol. IV., p. 152, 1878; Vol. V., pp. 34, 135, 145, 1879.

[8] One criticism may be made on Pisati's experiments. He employed the method of torsional oscillations, using wires about 70 cm. long; for such short wires the uncertain distribution of stress at the points of support may have an influence appreciable within his limits of error.

The low temperatures now available for scientific work make possible an extension of this study of elasticity as influenced by temperature, previously carried on above, but not below, ordinary temperature.

Some of the mechanical properties of matter have already been investigated at liquid air temperature. The ultimate tensile strength of a number of metals was measured by Dewar,[1] who found it greatly increased in most cases, the increase of strength being accompanied by decreased elongation at rupture; decreased elongation appears to accompany the increased strength due to low temperature, much as it accompanies at ordinary temperature the increased strength in iron and steel, due to the presence of other substances in chemical combination or as alloys.

Dewar made no quantitative determinations of the elastic moduli, however, although he mentions several experiments which indicate an increase of elasticity at low temperature. Thus a rod of fusible metal, supported at one end and loaded at the other, offered such resistance to flexure as to indicate a value of Young's modulus four or five times that at ordinary temperature. A spiral of fusible metal wire, which would be pulled straight by an ounce weight at ordinary temperature, supported two pounds at liquid air temperature, and vibrated like a steel spring; thus showing greatly increased modulus of rigidity. Dewar attempted to measure the rigidity modulus of steel by means of a spiral spring, but could detect no change; my experiments show a slight increase. The greatly increased rigidity of rubber is familiar to every one who has used liquid air.

There is no reason, however, to expect that most substances increase in elasticity at liquid air temperature as much as fusible metal or rubber. The metals of Pisati's experiments without exception decreased in rigidity with rising temperature, but at a rate that *increased* with the temperature. The change of rigidity with temperature is then less as a solid is further from its melting point. Furthermore, Pisati's results for different substances at the same temperature show in general a smaller rate of change, as the sub-

[1] James Dewar: Scientific Uses of Liquid Air. Proc. Roy. Inst., Vol. XIV., pp. 393–404, 1894.

stance is farther from its melting point.[1] If we may extrapolate from Pisati's results, we should expect a substance like iron which melts about 1600° C., to increase much less in rigidity at liquid air temperature than Dewar's fusible metal, whose melting point may have been below 200° C.

This reasoning appears confirmed by direct measurement of the elasticity of copper and steel wires at liquid air temperature.

Results of Experiments.

Each of the numerical values about to be submitted represents only a single complete determination.[2] Unavoidable circumstances prevented continuing the experiments so as to verify by repeated trials the results obtained, or to make determinations with other substances than copper and steel. It seems worth while, however, to put the experiments on record, even though the results are not numerous, and can not claim the same reliability as if there had been an opportunity to repeat the determinations.

The numerical values given below were obtained from wires approximately one meter long and 1.5 mm. in diameter. Young's modulus was determined by micrometer measurement of the extension under known tension; the modulus of rigidity by measurement of the statical twist due to a known torque; a detailed description of the apparatus follows later. In determining Young's modulus, the tension was varied approximately from 3 to 11 kgs. weight per square mm. For the rigidity modulus, the torque was varied from

[1] I have computed the accompanying table from Pisati's values: the first column of figures gives the melting point, the second gives the change in rigidity modulus per degree Celsius at 0°, expressed in percentage of rigidity modulus at 0° C.; that is, $\frac{100}{R_0} \cdot \frac{\partial R}{\partial T}$, where R is the modulus of rigidity, and T the temperature.

Aluminum,	600°–650° C.	0.064
Brass,	910	0.035 –0.039
Silver,	920–1040	0.027 –0.041
Gold,	1035–1250	0.0204
Copper,	1050–1330	0.023 –0.025
Steel,	1300–1400	0.0195
Iron,	1500–1800	0.0207
Platinum,	1765–2200	0.012 –0.015

[2] Except that of Young's modulus for copper, which was determined twice with the same wire. The two results differed by 3 per cent.

100 to 300 dyne-centimeters per centimeter of length, the (constant) tension being about 11 kgs. weight per square mm.

Denoting by Y_T and R_T Young's modulus and the rigidity modulus at the temperature $T°$ C., the experiments give the following results:

For the copper wire (hard-drawn), making no allowance for thermal contraction,

$$Y_{-186} = Y_{21} \times 1.177 \pm 0.020,^{1}$$
$$R_{-186} = R_{21} \times 1.063 \pm 0.003.$$

For the steel wire (piano wire),

$$Y_{-186} = Y_{21} \times 1.085 \pm 0.007,$$
$$R_{-186} = R_{20} \times 1.072 \pm 0.006.^{2}$$

By correcting for thermal contraction, these values are slightly modified; but the change in them is of the same order as the probable errors, so that it is not necessary to know the coefficients of thermal expansion at low temperatures with extreme accuracy, provided we can be sure they do not increase greatly with decreasing temperature. There is no reason to expect such an increase. The experiment of Zakrzewski[3] extending to $-103°$ C., show diminished coefficient of expansion with decreasing temperature. By extrapolation from his results the average coefficient of expansion of copper between 20° and $-186°$ may be taken as 0.0000156, and that of iron as 0.0000105. Using these values, we obtain the corrected ratios:

For the copper wire:

$$Y_{-186} = Y_{21} \times 1.180,$$
$$R_{-186} = R_{21} \times 1.073.$$

For the steel wire

$$Y_{-186} = Y_{21} \times 1.087.$$
$$R_{-186} = R_{20} \times 1.079.$$

[1] The $\pm$ refers on'y to the accidental errors, and takes no account of the systematic error mentioned on page 24.

[2] These ratios refer to the values at room temperature *before* cooling; those *after* cooling differed slightly. See page 23.

[3] J. Zakrzewski: Der Ausdehnungskoeffient fester Körper bei tiefen Temperaturen. Bull. de l'Acad. de Cracow, 1889. Abstract in Die Fortschritte der Physik, 1889.

According to the theory of elasticity, Poisson's ratio ($\varkappa$) is expressible in terms of Young's modulus and the modulus of rigidity by the formula[1]

$$\varkappa = \frac{Y - 2R}{2R}.$$

From this equation we find for the copper wire $\varkappa_{-186} = 1.098\varkappa_{20} + 0.098$; and for the steel wire $\varkappa_{-186} = 1.008\,\varkappa_{20} + 0.008$. Poisson's ratio then is greater than at ordinary temperature.

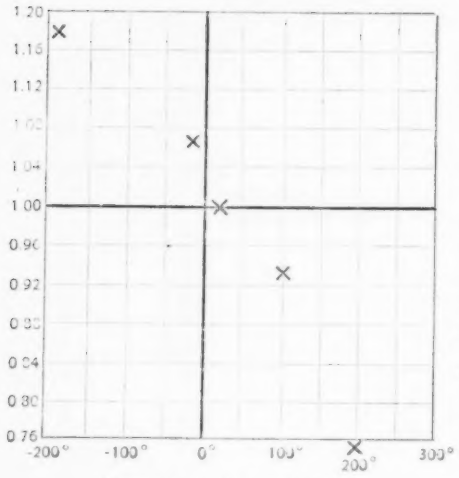
Comparison with the Value of Elasticity at Other Temperatures.

The mechanical properties of matter in the solid state vary with different specimens of the same substance. Accordingly our numerical values, obtained from a single copper wire and a single steel wire, must be considered as representing simply the behavior of those two particular wires, and not that of copper and steel in general; these values can at best furnish but rough indications of what may be expected with other copper and steel wires. This is more particularly the case because the wires did not undergo special treatment to reduce them to normal elastic condition, such as repeated heating and cooling, which would have been too wasteful of liquid air.

Nevertheless it is interesting to compare the variation of elasticity in these wires with that observed in other wires at higher temperatures by Pisati and Wertheim. I have accordingly plotted some of the values obtained by these observers, together with my own for liquid air temperature (Figs. 1–4, page 22). Regarding the modulus of rigidity, however, it must be remembered that in my experiments torsion took place isothermally, while in Pisati's it must have taken place nearly adiabatically, as the period of torsional oscillations was less than two seconds.

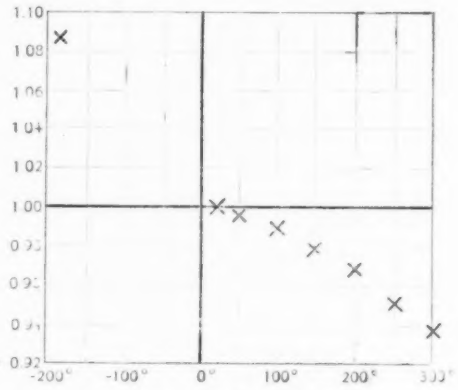
It will be seen that my results are not greatly different from those which would be obtained by extrapolation from the values of Pisati and Wertheim, except in the case of Young's modulus for steel, which is considerably greater at −186° than would be expected

[1] This formula assumes homogeneity, an assumption which is but imperfectly fulfilled in drawn wires.



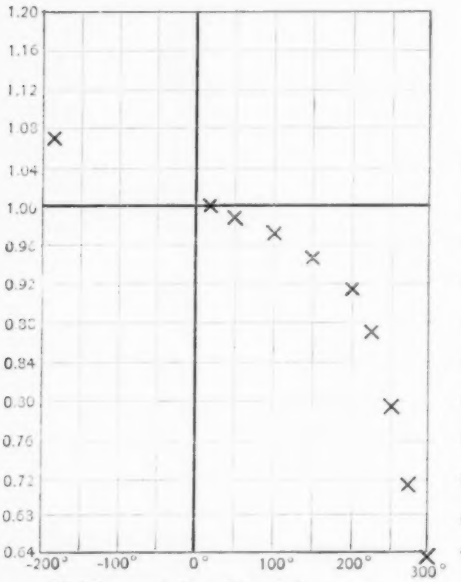
Young's modulus of copper,
in terms of its value at 20° C.
Wertheim's results for high temperatures.
My result for −186° C.

Fig. 1.



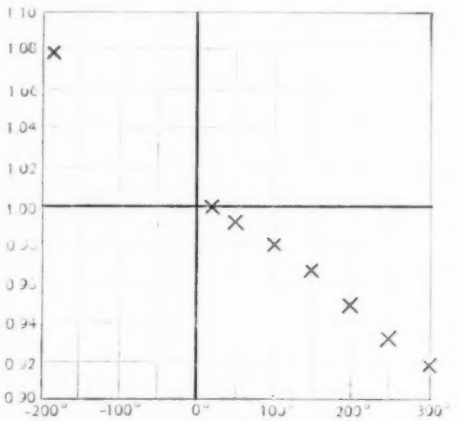
Young's modulus of steel,
in terms of its value at 20° C.
Pisati's results for high temperatures.
My result for −186° C.

Fig. 2.



Rigidity modulus of hard-drawn copper,
in terms of its value at 20° C.
Pisati's values for high temperatures.
My result for −186° C.

Fig. 3.



Rigidity modulus for steel,
in terms of its value at 20° C.
Pisati's results for high temperatures.
My result for −186° C.

Fig. 4.

from Pisati's experiments. My result, corresponding to an average increase of about 0.04 per cent. per degree C., seems more in accordance with the rather vague statement of Styffe,[1] that Young's modulus for steel increases with decreasing temperature not more than 0.03 per cent., or at most 0.05 per cent. per degree C.

Annealing Effect of Liquid Air.

Wertheim[2] observed that subjecting metals to low temperature (— 15° C.) leaves a residual effect, similar to that due to annealing when they are heated. The same phenomenon was observable in my experiments. Thus the modulus of rigidity of the copper wire after cooling to — 186° and warming again to room temperature, was less than it had been before, in the ratio of $0.974 \pm 0.003 : 1$, while that of the steel wire was greater in the ratio of $1.022 \pm 0.005 : 1$. Sudden cooling from high to ordinary temperature anneals copper and hardens steel; it appears that the same effect occurs in copper as a result of sudden cooling from ordinary to very low temperature, since the modulus of rigidity of copper decreases with annealing.[3] From the general impression that the modulus of rigidity of steel is increased by hardening, it would be easy to conclude also that steel is hardened by sudden cooling to — 186°; recent experiments, however, show that the rigidity is slightly decreased, instead of increased, by hardening.[4] From this it would appear that steel is not hardened, but annealed, by sudden cooling from ordinary temperature; but the data are not sufficient to draw general conclusions.

Description of the Apparatus for Young's Modulus.

The arrangement used to determine Young's modulus is shown in Fig. 5, which is not drawn to scale, but is simply a diagram; some of the dimensions being exaggerated, and front and side elevations being combined in one figure.

[1] Knut Styffe: Jern-Kontorets Annaler, XXI., pp. 11–64, 1866. Abstract in Dingler's Polytechnisches Journal, CLXXXV., pp. 205 and 282, 1867. Also in Kent's Mechanical Engineer's Pocket-Book.

[2] Pogg. Ann., Ergänzungsband II., pp. 1–115.

[3] Effect of Drawing on the Elasticity of Copper Wire. J. R. Benton, Phys. Rev., XIII., 4, pp. 234–245, 1901. See also the researches of Wertheim and Pisati.

[4] Prof. Thos. Gray: Effect of Hardening on the Rigidity of Steel. Science, New Series, Vol. XVI., p. 337, 1902.

A was a strong bracket fastened firmly to the wall; the wire *B*, *B* passed through a hole in *A* and was held there by a set-screw. *C*, *C* was an iron pipe, through which the wire hung; it was one half inch in external diameter, and 90 cm. in length. On its lower end was soldered a chuck *D*, which was screwed up so as to grip the wire, and at the same time close the end of *C*. The extension of the wires under varying stress was measured with micrometer microscopes, placed at *E* and *F*; the distance between the marks on which they were sighted was about 98 cm. When the wire was cooled with liquid air, thick frost deposited rapidly, and obscured the marks; this difficulty was overcome by fastening on the wire little air-tight vessels *G*, *G*, containing calcium chloride, and closed by plane glass on the side towards the micrometers. The marks were illuminated by light from a distant gas flame, focused upon them by lenses. The stretching forces were applied by the weights *H*, acting through the lever *I*, of mechanical advantage five fourths. *J*, *J* were rigid shelves for supporting the micrometers. Liquid air was introduced into the pipe *C* from the Dewar bulb *L* by means of a force-pump arrangement *M*, devised by Dr. J. S. Shearer. *K*, *K* was a glass tube, reaching to about 50 cm. from the bottom of *C*.

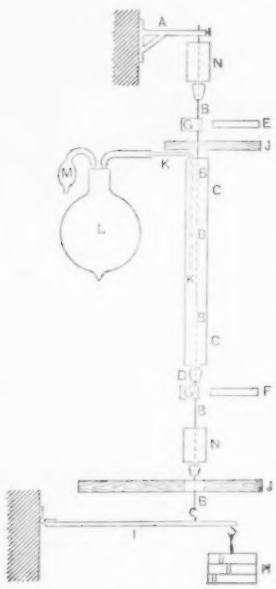


Fig. 5.

In order that the points on the wire at *E* and *F* should have the same temperature as those within *C*, the short tubes *N*, *N* were fastened on the wire. The intention was to keep them full of liquid air; I did not succeed, however, in securing a suitable arrangement for keeping them filled; they were empty during my observations, which are accordingly subject to error to the extent that part of the wire between *E* and *F* was not as cold as that within *C*. Of the total length between *E* and *F*, about eleven twelfths was within *C*.

When the pipe *C* was filled with liquid air, the tension of the wire being constant, it was found that the marks at *E* and *F* slowly moved up and down in an irregular manner, owing presumably to irregular thermal expansion and contraction in the wire above *E*, according as it was warmed by air currents from the room or cooled by the air boiling off at the top of *C*. To measure the extension under these conditions, the following procedure was adopted.

With a given load on *H*, a reading was taken at *F*; the instant it was obtained an assistant changed the load on *H*, and a reading at *F* with the new load was taken. The time required for such a pair of readings was less than ten seconds. The difference between the two readings gives the depression of the point *F*; by taking the two readings of a pair rapidly, concordant results for the depression were obtained, although the reading for the same load fluctuated continually. Ten such pairs of readings were taken for the lower micrometer; then ten were taken similarly for the upper one; the difference of depression at *E* and at *F* gives the elongation of the wire between *E* and *F*.

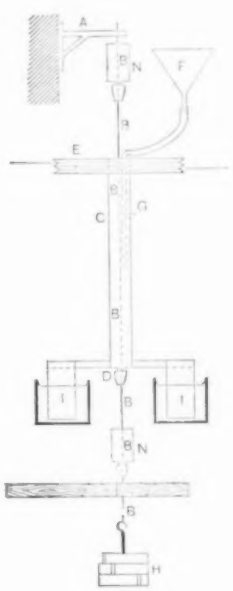


Fig. 6.

Apparatus for the Modulus of Rigidity.

In researches on the modulus of rigidity the method of torsional oscillations has been employed almost exclusively, on account of its great convenience and accuracy, as compared with other methods. In my experiments, where the wire hung through a tube filled with rapidly evaporating liquid, the method was clearly impracticable; I therefore used a statical method.

The apparatus is shown in Fig. 6, which, like Fig. 5, is merely diagrammatical. The method of suspension from *A*, and the tubes *C* and *N*, *N*, are the same as used for Young's modulus. To the top of *C* was rigidly fastened a horizontal wooden pulley *E*, 24 cm. in diameter. Liquid air was introduced into the pipe *C* by means of a glass tube *G*, which was

connected to a funnel F, supported on the pulley E, and free to turn with it. In order to damp torsional oscillations, the two vanes I, I, dipping in vessels of glycerine, were clamped to the lower end of C. Besides the apparatus shown in Fig. 6, there was at the top of the wire a torsion-head arrangement; and at the bottom of C a system of counterpoise weights for bringing the center of gravity of C below its point of attachment to the wire.

The arrangement for applying a constant twisting moment to the wire is shown on a smaller scale in Figs. 7 and 8. Light flexible threads, a, a, were fastened at one end to opposite sides of the rim of the pulley E, at the other end to the walls of the room about 70 cm. above E. The distance from C to each wall was about 2 meters. About 1 meter from C, on each side, very light scale-pans b, b were fastened on the thread. If weights were placed on these scale-pans a couple acted on the pulley E, by reason of the increased horizontal pull in a, a; E accordingly turned until the couple was balanced by torsion of the wire. To determine the absolute value of this couple, accurate knowledge of the various distances and of the weight of the thread would have been necessary. Since, however, the purpose of the experiments was simply to *compare* the torsional elasticity at $-186°$ C. with that at ordinary temperature, it was not necessary to know the absolute value of the couple, but only to be able to apply the same couple at different times.

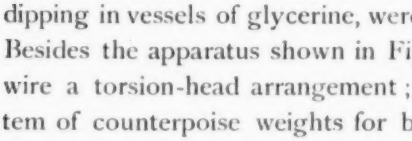


Fig. 7.

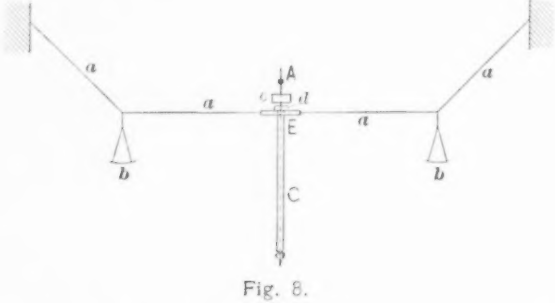


Fig. 8.

To measure the angle through which the wire was twisted a vertical plane mirror d (Fig. 8) was fastened to the pulley E.

Since E was rigidly fastened to the pipe C, which in turn was fastened to the lower end of the wire, d turned through the same angle as the lower end of the wire. A second vertical plane mirror e (Fig. 7) was clamped to the wire itself just above the top of C. By means of lenses the light of a gas burner passing through a narrow slit was brought to a focus after reflection from the mirrors d and e, so that two images of the slit were cast upon a scale 359 cm. distant from the wire and 4 meters in length. By reading the distances through which these images were displaced by the addition of weights to the scale-pans b, b, the angles through which the mirrors d and e turned could be computed; the difference between them gives the angle of twist of the wire.

The apparatus was used in the following manner: Weights were chosen, which when placed in the scale-pans b, b, twisted the wire about 12°. A set of twenty readings was made at room temperature, alternately with and without these weights in the scale-pans; the position of the wire was slightly varied two or three times during the set by means of the torsion head at its upper end. Then the pipe C was filled with liquid air, and the same process was repeated, using the same weights. If R_T is the modulus of rigidity and a_T the angle of twist at temperature $T°$ C., then we have

$$R_{-186} = R_{20} \times \frac{a_{20}}{a_{-186}},$$

making no allowance for thermal contraction. After the wire had returned to room temperature, another set of readings was taken.

My thanks are due to Mr. K. P. Beardslee, of Cornell University, for assistance in taking the readings for Young's modulus.

Cornell University, June, 1902.

GENERALIZATION OF CARNOT'S CYCLE.

BY SANFORD A. MOSS.

THE ideal heat engine cycle proposed by Carnot comprises the following operations: adiabatic compression from absolute temperature T_0 to T_1, then addition of heat at constant temperature, next adiabatic expansion, and finally extraction of heat at constant temperature until the cycle is closed. The "efficiency" of this cycle, that is the ratio of the mechanical work done by the working substance, to the heat added, is well known to be $e = 1 - T_0/T_1$.

We shall show that the same expression for efficiency holds for the more general cycle in which the addition and extraction of heat are carried on with varying temperatures, provided that the "specific heat" has the same constant value during these periods. The operations performed on the working substance will then be as follows: adiabatic compression from absolute temperature T_0 to T_1, then addition of heat during expansion so conducted that the temperature varies directly with the heat added, that is, expansion with "constant specific heat," next adiabatic expansion, and finally extraction of heat with constant specific heat of the same magnitude as during addition of heat.

Before proceeding with the proof of this statement we shall consider the operation of adding heat with "constant specific heat." While a quantity of heat dQ is being added to unit mass of any substance, the volume may at the same time be varied an arbitrary amount dv, so that external work is done having an arbitrary value $1/J\,pdv$. The difference between dQ and $1/J\,pdv$ goes to increase the internal energy of the body and the temperature may therefore increase an amount dT. Since dQ and $1/J\,pdv$ are independent we may make their difference such that dT will have any value that we choose. That is, the value of dQ/dT may be made anything we please if we assign an appropriate value to dv/dQ. Now dQ/dT is

the "specific heat" and dv/dQ is the rate of expansion during addition of heat. Hence by properly varying the rate of expansion, we may make the specific heat assume any desired series of values. As a particular case the rate of expansion dv/dQ may be so adjusted that the specific heat dQ/dT has any desired constant value while heat is being added. The line on a "pv" diagram representing such an expansion we may call a "line of constant specific heat."

For solids, lines of constant pressure are approximately lines of constant specific heat. For a perfect gas the curve $pv^n = \text{constant}$ is a line of constant specific heat, n having any value whatever. Although this fact is well known, the following brief proof will not be amiss. A perfect gas is defined as one obeying the relations $pv = RT$ and $dQ = cdT + 1/J\,pdv$ where c is a constant called the "specific heat at constant volume." From the relations $pv = RT$ and $pv^n = \text{constant}$, we have

$$pdv + vdp = RdT$$

$$npdv + vdp = 0.$$

By subtraction

$$pdv = \frac{RdT}{1 - n}.$$

Hence

$$dQ = cdT + \frac{R}{J(1 - n)}dT.$$

Therefore

$$\frac{dQ}{dT} = c + \frac{R}{J(1 - n)}.$$

This is constant and therefore the curve $pv^n = \text{constant}$ is a line of constant specific heat for a perfect gas for any value of n. For $n = 0$ we have a line of constant pressure, for $n = \infty$ a line of constant volumé, for $n = 1$ an isothermal line and for $n = c_p/c = k$ an adiabatic. These are therefore all lines of constant specific heat. As actual gases depart slightly from the perfect gas laws lines of constant specific heat for them will be curves $pv^n = \text{constant}$ where n is not a constant but varies slightly during expansion. The isothermal curve or line of constant temperature, for any substance

whatever, is a line of constant specific heat since dQ/dT has the constant value ∞.

With this consideration of the properties of lines of constant specific heat we will return to the discussion of the generalized heat engine cycle. Let 0123 be the pv diagram of a heat engine cycle,

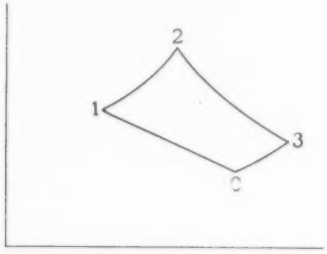


Fig. 1.

any working substance whatever being used; where 01 and 23 are adiabatics and 12 and 03 are any lines of constant specific heat, with the same value of dQ/dT. Let T be the variable value of the absolute temperature at any point in the cycle and let dQ be the corresponding increment of heat per unit mass. From 0 to 1 dQ is always zero as the compression is adiabatic. From 1 to 2 an amount of heat $\int_1^2 dQ$ is added and this is the amount of energy supplied to our heat engine. From 2 to 3 there is adiabatic expansion and dQ is again zero. From 3 to 0 heat is extracted or a negative amount of heat is added $\int_3^0 dQ$. The mechanical work done by the engine is the area of the cycle diagram and this must be equal to the algebraic sum of the amounts of heat added during the various events, by the law of conservation of energy. Hence the efficiency of the cycle is

$$e = \frac{\int_1^2 dQ + \int_3^0 dQ}{\int_1^2 dQ}.$$

Since all of the heat is added along curves of constant specific heat

and since the value of the specific heat is the same throughout we have $dQ = CdT$. Hence the expression for efficiency may be written

$$e = \frac{\int_1^2 CdT + \int_3^0 CdT}{\int_1^2 CdT}$$

$$= \frac{T_2 - T_1 + T_0 - T_3}{T_2 - T_1}$$

$$= 1 - \frac{T_3 - T_0}{T_2 - T_1}$$

$$= 1 - \frac{T_0}{T_1}\left\{\frac{\frac{T_3}{T_0} - 1}{\frac{T_2}{T_1} - 1}\right\}.$$

We may simplify this expression by means of a relation deduced from the application of the second law of thermodynamics to our cycle. As we have a closed reversible cycle we may write

$$\int \frac{dQ}{T} = 0$$

the integration being made over the whole cycle. This becomes therefore

$$\int_1^2 \frac{dQ}{T} + \int_3^0 \frac{dQ}{T} = 0.$$

Since we have always $dQ = CdT$,

$$\int_1^2 \frac{CdT}{T} + \int_3^0 \frac{CdT}{T} = 0$$

or
$$\log \frac{T_2}{T_1} = \log \frac{T_3}{T_0}$$

or
$$\frac{T_2}{T_1} = \frac{T_3}{T_0}.$$

Substituting this relation in our expression for the efficiency, we obtain

$$e = 1 - \frac{T_0}{T_1} = \frac{T_1 - T_0}{T_1}.$$

This is at once recognized as the value of the efficiency of a Carnot's cycle. In fact Carnot's cycle is included in the general class of cycles considered since the lines of addition and extraction of heat, being isothermals, are lines of constant specific heat for which dQ/dT has the same value, viz., ∞. For this reason we may call the general cycle we have been considering a "generalized Carnot's cycle."

We have shown therefore that all heat engines having adiabatic compression from T_0 to T_1 and addition and extraction of heat along any lines with the same constant specific heat; have the efficiency $1 - T_0/T_1$.

The temperature variations during the time heat is added or taken away have no influence on the efficiency. It is often supposed that the efficiency of heat engines always increases with the maximum temperature, but this is seen to be erroneous, and cycles of the class considered have the same efficiency whether the temperature is constant or is raised to any value whatever during addition of heat.

We have developed our efficiency theorem for a heat engine using any working substance whatever. It will be worth while to give an independent proof for the case where the working substance is a perfect gas. As we have shown, the curves pv^n = constant are lines of constant specific heat for a perfect gas. Zeuner has called these "polytropic curves." Our theorem therefore assumes the following form. A heat engine using a perfect gas with a cycle formed by two adiabatic crossed by two polytropic curves with the same index, has the efficiency $1 - T_0/T_1$ where T_0 and T_1 are the initial and final temperatures of the adiabatic compression. This theorem was announced some time ago by Röntgen, but it is not generally known to students of thermodynamics. The following proof is believed to be new.

Let the previous figure represent the pv diagram of the cycle, 01 and 23 being adiabatics and 12 and 03 curves of the form $pv^n =$

constant. Let Q be the total heat per unit mass added from 1 to 2 and q the heat extracted from 3 to 0. We have already established the following relation for a perfect gas :

$$dQ = \left\{ c + \frac{R}{J(1-n)} \right\} dT.$$

Hence

$$Q = \int_1^2 dQ = \int_1^2 \left\{ c + \frac{R}{J(1-n)} \right\} dT$$

$$= \left\{ c + \frac{R}{J(1-n)} \right\} (T_2 - T_1).$$

In the same way we may obtain

$$q = \left\{ c + \frac{R}{J(1-n)} \right\} (T_3 - T_0)$$

Since the value of n is the same for both cases,

$$\frac{Q}{q} = \frac{T_2 - T_1}{T_3 - T_0} = \frac{T_1}{T_0} \left| \frac{\frac{T_2}{T_1} - 1}{\frac{T_3}{T_0} - 1} \right|.$$

Since 1 and 2 are on the same polytropic curve

$$p_1 v_1'^n = p_2 v_2'^n.$$

Similiarly

$$p_0 v_0'^n = p_3 v_3'^n.$$

By division

$$\frac{p_1}{p_0} \left(\frac{v_1'}{v_0'} \right)^n = \frac{p_2}{p_3} \left(\frac{v_2'}{v_3'} \right)^n.$$

Since 0 and 1 are on the same adiabatic we have by a well-known relation

$$\frac{p_1}{p_0} = \left(\frac{T_1}{T_0} \right)^{\frac{k}{k-1}} \quad \frac{v_0'}{v_1'} = \left(\frac{T_1}{T_0} \right)^{\frac{1}{k-1}}$$

where k is the ratio of the specific heat at constant pressure to the specific heat at constant volume.

Hence

$$\left(\frac{v'_1}{v'_0}\right)^n = \left(\frac{T_1}{T_0}\right)^{\frac{-n}{k-1}}.$$

Therefore

$$\frac{p_1}{p_0}\left(\frac{v'_1}{v'_0}\right)^n = \left(\frac{T_1}{T_0}\right)^{\frac{k}{k-1}-\frac{n}{k-1}}.$$

In the same manner we may show

$$\frac{p_2}{p_3}\left(\frac{v'_2}{v'_3}\right)^n = \left(\frac{T_2}{T_3}\right)^{\frac{k}{k-1}-\frac{n}{k-1}}.$$

Hence

$$\frac{T_1}{T_0} = \frac{T_2}{T_3} \text{ or } \frac{T_2}{T_1} = \frac{T_3}{T_0}.$$

By means of this relation we may simplify our expression for Q/q. We then obtain

$$\frac{Q}{q} = \frac{T_1}{T_0} \text{ whence } 1 - \frac{q}{Q} = 1 - \frac{T_0}{T_1}.$$

Hence

$$\frac{Q-q}{Q} = \frac{T_1 - T_0}{T_1} = 1 - \frac{T_0}{T_1}.$$

Since $Q - q$ is the mechanical work obtained from the engine, the ratio of $Q - q$ to Q is the efficiency. That is

$$e = 1 - \frac{T_0}{T_1}.$$

This result for the special case of a perfect gas agrees with the result for the general case, as of course it should.

An important application of the theorem we have developed is as follows: Gas engines or "internal combustion" engines, and hot-air engines use a working substance which may be considered as a perfect gas. Hence when heat is added and extracted at constant volume, as in the "Otto" gas engine or Stirling air engine, or when heat is added and extracted at constant pressure, as in the Brayton gas engine or Joule air engine, the efficiency is the same as for a Carnot engine with the same range of compression temperatures.

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SOME OPTICAL PROPERTIES OF IODINE.

By William Weber Coblentz.

IODINE is an interesting example of apparently several allotropic states. At low temperatures iodine vapor[1] gives a banded absorption spectrum from red to violet. As the temperature increases, absorption in the blue and violet increases, and finally becomes continuous. At still higher temperatures blue and violet are again transmitted and bands appear.

The relation of the spectra of chlorine and bromine gases[2] to that of iodine has also been extensively investigated. It has been found that for the halogen group the absorption lines shift toward the red with increasing atomic weight.

According to Gänge[3] iodine is the only element which distinguishes itself by peculiar properties towards two groups of solvents. The first group, to which belong water, the alcohols, ethers, etc., with increasing concentration, dissolves iodine with a yellow to a dark brown color. In this group the solutions appear in colors which resemble closely those of solid and liquid iodine by transmitted light. The second group, to which belong carbon bisulphide, chloroform, benzol, etc., dissolves iodine with a violet color, which resembles more nearly that of the vapor, and gives the same spectrum. Hence, the molecular arrangement in the first group of solutions is assumed similar to that of solid and liquid iodine, and in the second group similar to that of the vapor.

The second group is also assumed to have a simpler structure. To test this the CS_2 solution was cooled in a mixture of solid carbon dioxide and ether. It became brown.[4] In solutions of

[1] Konen, Wied. Ann., 65, p. 258 (1898), gives a very complete bibliography of work done on iodine vapor — both emission and absorption spectra. See also Kayser, Spectralanalyse, p. 284.

[2] E. Laird, Astrophys. Jour., Sept., 1901, for bibliography.

[3] Gänge, Lehrbuch der angewand. Optik in der Chemie, p. 225.

[4] E. Wiedemann, Sitzber. Phys. Soc. Erlangen, 1887.

iodine in carbon bisulphide above the critical temperature, where the state approximates that of a gas, but the density that of a liquid, Wood[1] found that a continuous or banded spectrum appeared according to the amount of the solvent. These bands seemed to appear only in the presence of an excess of free iodine and each aggregation apparently caused a change of spectrum.

Of a different nature is Tyndall's ingenious work on the diathermancy of iodine in carbon bisulphide. He discovered this property for the infra-red rays[2] in 1865, and "to make radiant heat an explorer of molecular conditions," he used the carbon bisulphide solutions to filter the obscure from the luminous rays.[3]

It is the purpose of the present paper to describe some experiments upon the optical properties of this interesting element. The work divides itself into four parts, viz.:

1. The study of the absorption spectrum of iodine in solution.
2. The study of the absorption spectrum of solid and liquid iodine. Comparison of the thickness of iodine as a film, and in solution.
3. Pleochroism of iodine.
4. Anomalous dispersion in solid and liquid iodine.

I. The Absorption Spectrum of Iodine in Solution.

So far as the writer is aware no recent or systematic investigations of the optical properties of iodine dissolved in carbon bisulphide have been made, although iodine solutions have been used in the determination of the radiant efficiency of various sources of light for nearly half a century.

Desain and Aymonet,[4] using a quartz prism and thermopile, report a "cold" band in the infra-red at an angle of 1° 30′ from the extreme red.

In 1883, H. Becquerel[5] found that a concentrated solution, 2.5 cm. in thickness, absorbed all the rays up to the A line and allowed the less refrangible to pass.

[1] Wood, Phil. Mag., 41, 1896.
[2] Tyndall, Poggendorf's Ann., Bd. 124 (1865).
[3] Tyndall, Contributions to Molecular Physics.
[4] Desain and Aymonet, Compt. Rend., 81, p. 423 (1875).
[5] H. Becquerel, Ann. Chem. et Phys. (5), 30 (1883).

In the following paragraphs it is proposed to describe measurements of the absorption spectrum of iodine solutions, which were made for the purpose of obtaining more definite information concerning these and other points.

1. *Measurements in the Visible Spectrum.*

In the study of the visible spectrum a "horizontal slit" spectrophotometer[1] was used. A series of thirteen solutions containing from 3.3 to 0.017 milligrams of iodine per cubic centimeter of carbon bisulphide was prepared, by dilution. Although not very economical, this method reduced the errors in the concentrations. The cell containing these solutions had thin walls of lantern slide glass. The thickness of the liquid layer was 1.5 centimeters.

Measurements of the transmitting power of these solutions were made for 19 different regions of the spectrum between 0.74 μ and 0.46 μ. The effect of the cell walls and of the solvent were eliminated by observations upon the cellfilled with clear carbon bisulphide. The absorbtion of iodine in the visible spectrum was found to consist of a single broad band with its maximum at wave-length $\lambda = 0.5\ \mu$, the transmission curve being steeper on the side towards the violet.

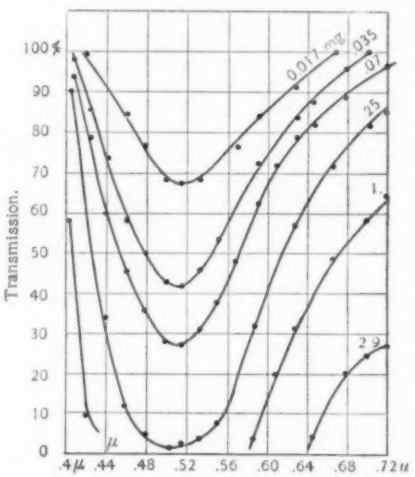

Fig. 1. Iodine in CS_2.

The gradual development of this absorption band is best indicated in Fig. 1, which shows the transmitting power throughout the visible spectrum of several solutions 1 cm. in thickness. The data for these curves were obtained by substituting the values given in Table I. in the formula $\frac{n}{m} \log \frac{I_0}{I_m} = \log \frac{I_0}{I_n}$, where n and m are the relative thicknesses, I_0 is the intensity of the incident and I_m is the

[1] E. L. Nichols, PHYSICAL REVIEW, Vol. II., p. 140.

transmitted light, and are given in Table II. For the weakest solution, 0.017 mg. per c.c., the transmission in the maximum of the band is about 64 per cent., which corresponds to a transmission of nearly 80 per cent. for a layer one centimeter thick. As the concentration increases the absorption band widens and becomes more dense, so that a solution of only 0.25 mg. per c.c. transmits only about 2 per cent. in the center of the band. All stronger solutions are opaque in this region, and as the concentrations increase this opacity extends, until finally the whole of the visible spectrum is absorbed. The strongest solution upon which it was found possible to make spectrophotometric measurements even in the red, contained 3.3 mg. per c.c.

TABLE I.

Transmission of Iodine in Carbon Bisulphide. Thickness of Cell = 1.5 cm.

Wave-lengths.	Transmission, $I_e \div I_0$.													
Conc. mg. per c.c.	3.3	2.9	2.0	1.6	1.3	1.0	0.7	0.5	.25	.13	.07	.035	.0175	Clear CS_2.
Normal Solutions.	$M = .012$	.0117	.0079	.0063	.0051	.0039	.0028	.00197	.00088	.00051	.00028	.00014	.00007	
.406 μ					.22	.43		.76	.86	.90	.91	.98	1.00	
.424					.07	.08		.17	.42	.61	.70	.86	.93	.98
.442					00	00		00	.20	.27	.45	.64	.83	
.46					0	0		0	.08	.19	.32	.47	.77	.96
.48					0	0		0	.04	.12	.24	.37	.70	.94
.50					0	0		0	.01	.10	.17	.30	.65	.90
.517					0	0		0	.02	.11	.16	.30	.63	.87
.534					0	0	0	0	.03	.12	.18	.34	.64	.83
.554					0	0	0	00	.06	.19	.26	.42	.68	.84
.57					0	00	00	.02	.12	.20	.36	.56	.74	.84
.59					00	.03	.03	.14	.20	.36	.53	.66	.80	.85
.61		0	00	00	.03	.11	.16	.24	.38	.51	.66	.80	.86	
.63	0	.01	.05	.08	.10	.19	.27	.35	.47	.64	.76	.84	.91	.88
.645	.01	.03	.08	.14	.20	.30	.40	.47	.60	.71	.81	.88	.94	.92
.665	.02	.06	.11	.18	.28	.38	.47	.54	.66	.74	.85	.93	.99	
.68	.04	.11	.15	.23	.33	.45	.53	.64	.72	.79	.89	.96	1.00	.95
.70	.04	.13	.18	.25	.37	.49	.55	.70	.78	.86	.93	.98	1.00	
.72	.06	.15	.22	.28	.41	.52	.62	.77	.81	.89	.95	.99	1.00	.99
.74	.09	.19	.25	.32	.45	.55	.66	.80	.87	.93	.97	1.00	1.00	

The percentages of light transmitted by the iodine in carbon bisulphide are given in Table I. From these values Table II. was obtained, which gives the transmission for solutions 1 cm. in thick-

ness. In these and the three following tables the concentrations are given in milligrams per cubic centimeter, and also as normal solutions.

TABLE II.

Transmission of Iodine in Carbon Bisulphide. For a layer 1 cm. in thickness. Computed from Table I.

Wave-lengths.	Transmission, $I_e \div I_0$.						Extinction Coefficients.					
Conc. mg. per c.c.	2.9	1.	0.25	0.07	.035	.017	2.9	1.	0.25	0.07	0.035	0.017
Normal Solutions.	.0117	.0039	.00098	.00028	.00014	.00007	.0117	.0039	.00098	.00028	.00014	.00007
.406 μ		.58	.91	.94	1.00			.545	.0924	.060		
.424		.09		.79	.86	1.00		2.410		.235	.151	00
.442		00	.34	.60	.74	.90		00	1.080	.510	.369	.105
.46		0	.12	.46	.59	.85			2.12	.779	.528	.165
.48		0	.05	.37	.50	.77			3.020	0.996	.697	.263
.50		0	.02	.28	.43	.69			3.900	1.271	.845	.372
.517		0	.03	.27	.42	.67			3.471	1.312	.868	.402
.534		0	.04	.31	.46	.69			3.230	1.171	.779	.372
.554		0	.08	.38	.53				2.530	.972	.635	
.57		00		.48		.77		00		.732		.263
.59		.04	.32	.62	.72	.84		3.230	1.142	.478	.328	.174
.61		.20		.72				1.610		.328		
.63		.31	.58	.79	.84	.92		1.171	.545	.235	.174	.084
.645	.04			.82	.88		3.230			.197	.128	
.665		.49	.72			1.00		.715	.328			
.68	.20			.89	1.00		1.010			.116		
.70	.25	.59	.82				1.388	.528	.193			
.72	.27	.64	.86	.96			1.312	.445	.151	.041		

The absorption of solutions of iodine in alcohol differs very markedly from that of iodine in carbon bisulphide. The solutions are far more transparent in the red and yellow, hence greater concentrations could be used. Measurements with the spectrophotometer show for all concentrations a rapidly increasing opacity toward the violet. This is best shown in Fig. 2 (obtained by computation like Fig. 1), where it will be noticed that a solution of 0.05 mg. per c.c. instead of being nearly transparent at $\lambda = .4\ \mu$, transmits only about 20 per cent. of the incident light. In the red, on the other hand, the opacity of the alcohol solutions is relatively much less than that of a corresponding solution in carbon bisulphide. For example, a solution containing 3.2 mg. per c.c. transmits

60 per cent. at $\lambda = .72\ \mu$, whereas the corresponding solution in CS_2 allows scarcely 6 per cent. of the incident light to pass through at that wave-length. The dilute alcohol solutions are dichroic, so that we have an increase in the amount of light transmitted in the region where the CS_2 solutions showed a maximum absorption. From the steepness of the transmission curves, Fig. 2, for the weaker solutions, which begin to trend sharply downward at about $\lambda = .50\ \mu$, one would infer the existence of an absorption band located in the ultra-violet.

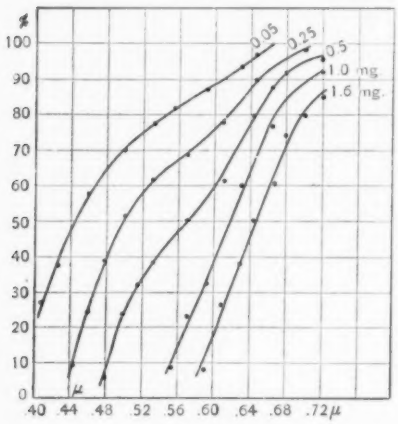

Fig. 2. Iodine in Alcohol.

The very different absorption of iodine in these two solvents is further exhibited in the isochromatic curves in Figs. 3 and 4, which show the increasing opacity of the various wave-lengths as the concentration increases. From the isochromatic curves, for solutions 1 cm. in thickness, where concentrations are plotted as abscissæ and transmission as ordinates, the transmission of normal solutions, $M = .01$, .001 and .0001, were obtained and are given in Table II*a*.

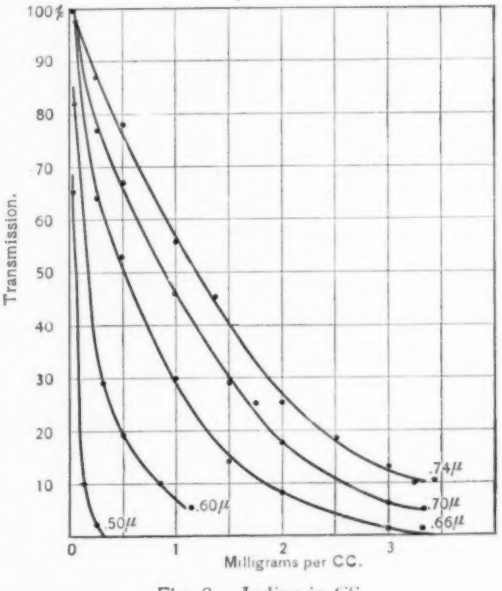

Fig. 3. Iodine in CS_2.

In Table IV. the transmission of alcohol solutions 1 cm. in thickness is given. These values were obtained from Table III. by com-

putation, in the same manner as for the carbon bisulphide solutions.

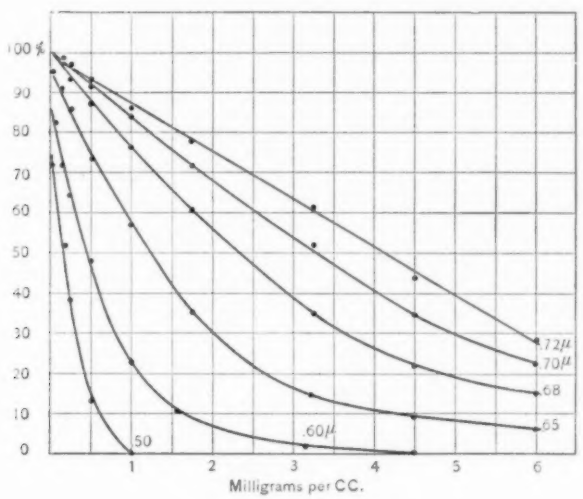

Fig. 4. Solution in Alcohol.

TABLE II*a*.

Transmission of Normal Solutions. Cell 1 cm. in Thickness.

Transmission of Carbon Bisulphide Sols. Normal Solutions ($M = 1$).				Transmission of Alcohol Sols. Normal Solutions ($M = 1$).		
Wave-lengths in μ.	$M = .01$.	$M = .001$.	$M = .0001$.	Wave-lengths in μ.	$M. = 001$.	$M = .0001$.
.50		2	42	.46	24	60
.56		13	64	.50	50	73
.59		30	72	.534	60	80
.60	0	38	77	.57	67	84
.64	7	60	87	.61	78	89
.66	18	69	93	.645	89	97
.68	24	75	96	.665	92	99
.70	29	82	99	.68	96	100
.72	32	85	100			

From the equation

$$I_e = I_0 e^{-kd}$$

the extinction coefficient,[1] k, was computed for a thickness, d, (= 1 cm.), using the percentages of light transmitted given in

[1] Ångström, Wied. Ann., 36, p. 715 (1889).

TABLE III.

Transmission of Iodine in Ethyl Alcohol. Cell 1.5 cm. in Thickness.

Wave-lengths.	Transmission, $I_e \div I_0$.									
Concentrations.	Clear Sol.	6 mg.	c.c. 4.5	3.2	1.6	1.0	0.5	0.25	0.13	0.5
Normal Solutions, $N = 1$.		$M = .024$	$M = .018$	$M = .013$	$M = .0063$	$M = .0039$	.00197	.00098	.00051	.0002
.406 μ	.94								.09	.15
.424								00	.16	.24
.442								.09	.26	.36
.460								.13	.35	.47
.48	.94						.04	.26	.43	.54
.50							.13	.39	.52	.63
.517	.96					00	.18	.45	.59	.67
.534						.04	.24	.51	.62	.70
.554	.96					.09	.29	.56	.66	74
.57					00	.12	.38	.59	.68	79
.59	.97				.07	.18	.44	.66	.73	.83
.61	.98			00	.14	.28	.50	.71	.78	.87
.63	.99	.02	.06	.08	.24	.47	.61	.76	.83	.91
.645		.05	.09	.13	.35	.54	.71	.85	.91	.96
.665	.99	.10	.14	.22	.47	.68	.83	.92	.96	.99
.68		.16	.24	.37	.64	.78	.89	.95	.97	.99
.70	1.00	.22	.35	.53	.72	.84	.92	.97	.99	1.00
.72		.28	.44	.61	.78	.87	.94	.97	1.00	

Tables II. and IV. The corresponding extinction coefficients are given in the same tables.

This work was performed at room temperature, —about 20° C.— on old and new solutions. The principal errors in such work are those introduced in handling the solutions, which evaporate readily, and those due to inaccuracies in the spectrophotometric comparisons, which depend in part upon the physical condition of the observer.

Observations in the Infra-red.

The Radiometer.—This instrument was built according to the design used by Nichols [1] and only the modifications to suit the work in hand need be described. The vanes were of mica blackened by burning camphor gum. To cause the lamp-black to adhere to the mica, a very thin coating of beeswax was first applied by means of a hot wire. When the vanes were held above the burning gum the

[1] E. F. Nichols, PHYSICAL REVIEW, Vol. 11, p. 891 (1897).

TABLE IV.

Transmission of Iodine in Ethyl Alcohol for a Layer 1 cm. in Thickness. Computed from Table III.

Wave-lengths.	Transmission, $I_e \div I_0$.					Extinction Coefficients.				
Concent'ns, mg. per c.c.	1.6	1.0	0.5	0.25	0.05	1.6	1.0	0.5	0.25	0.05
Normal Solutions.	$M = .0063$	.0039	.00197	.00098	.0002	.0063	.0039	.00197	.00098	.0002
.424 μ					.38					.972
.460				.25	.58				1.389	.545
.50			.24	.52	.71			1.430	.655	.343
.517			.32					1.150		
.534			.38	.62	.77			.972	.478	.263
.554		.09			.82		2.410			.198
.57		.23	.50	.69			1.470	.697	.372	
.59	.08	.32			.87	2.530	1.150	.500		1.39
.61	.27		.61	.78		1.312		.496	.249	
.63	.38	.60			.93	.972	.510			.072
.645	.50		.80	.90	.97	.697		.226	.106	.034
.665	.60	.77	.88			.510	.263	.128		
.68	.74	.85	.92	.96	1.00	.369	.165	.0835	.041	00
.70	.80			.98		.226			.020	
.72	.85	.92	.96			.165	.0835	.041		

wax softened, and the soot deposited in an even layer. The inner window was of mica while the outer one was of plate glass.

The quartz fiber suspension was purposely chosen of medium weight to avoid the effects of temperature changes and earth tremors. There seems to be no criterion for selecting a fiber. Experience shows that a fiber about 8 cm. long, which will float freely in still air without bending over, is a good one to begin with. Such a fiber is quite invisible when held in the light on a cloudy day. The one used in this work was of such a nature, and observations could be made at any time of the day without being affected by outside disturbances. The drift of the zero reading was small, never greater than 1.5 mm. during one reading. Electrification of the vanes in exhausting was the only source of annoyance. This electrification was found greatest, *i. e.*, the vanes were attracted to the mica window the longest, for newly blackened vanes. The vanes no doubt become electrified in handling. The most effective treatment was to wipe off the mica window with alcohol or, better still, with

water, just before exhausting. This trouble was avoided to some extent by exhausting slowly, and during the latter part of the work, by covering the mica window with tinfoil. The spectrometer slits were .4 mm. wide and the maximum deflection, as read on a scale at a distance of 1.5 m., was 40 + cm. The pressure, measured by a McLeod gauge, was about .08 mm. and the period was such that the maximum deflection was reached in 16 seconds.

The Spectrometer. — A mirror spectrometer was used. The mirrors were of 14 centimeters focal length, 6 cm. aperture, and were in good condition. The arrangement of the apparatus is shown in Fig. 5, in which F_1 is the collimator slit; C is the cell containing the solution; S, a double screen which could be interposed or removed by the observer at the reading telescope; P, the carbon bisulphide prism; and R, the radiometer. To a bracket, rigidly attached to the collimator tube, a cylindrical flame acetylene burner was mounted, with its center directly behind the collimator slit. In order to avoid the inconvenience of shifting the radiometer in exploring the spectrum, the arm carrying the mirror and the slit, F_2, which is placed at the vertical focus of the refracted ray, was clamped rigidly and placed in line with the radiometer. This makes the radiometer and spectrometer each a system by itself, and the shifting of either will simply vary the total amount of energy falling upon the vanes.

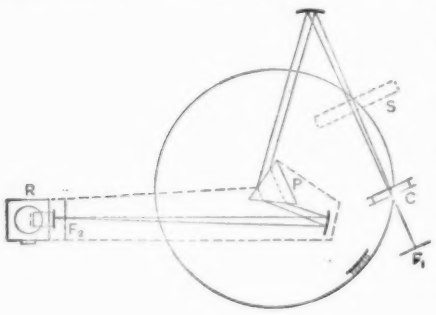

Fig. 5.

The spectrometer and radiometer were rigidly fixed upon a heavy slate slab. A bit of white paper on the rear wall of the radiometer indicated whether all the incident light fell upon the mica vane. The sensitiveness of the radiometer was varied by means of the leveling-screw opposite the window, and also by means of the exhaust pump.

In this work ratios are dealt with, and the only errors due to shifting would occur during two successive readings. The consistent

results of successive settings leads to the conclusion that no such shifting occurred. This is best graphically illustrated in Fig. 6, which shows the constancy of the point of maximum deflection. The data for these curves are selected at random from the notebook. They extend over several months, and originally were not taken to illustrate this point.

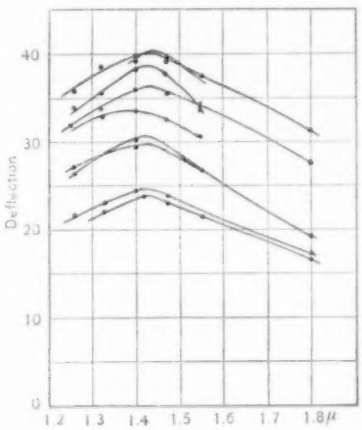

Fig. 6.

The prism was set for minimum deviation of the D lines by means of a telescope. By moving the collimator which carried the light, different portions of the spectrum ould be brought on the radiometer.

Changes of temperature are negligible, since it is known that for a carbon bisulphide prism a change of temperature of 5° is necessary to bring the D_1 line in the place of D_2.[1] The temperature of the prism was observed at the beginning and at the end of each series of measurements. It was found that during a single series of observations, which took from 30 to 50 minutes, the variation was only about 0°.3 C., the maximum recorded being 0°.6 C. The temperature of the room was fairly constant at 18° C. in the morning, rising to 19° or 20° in the afternoon. The solutions stood on an open shelf in the same room and were assumed to be at the same temperature.

Calibration.—The spectrometer was calibrated by using Snow's[2] values for the position of the sodium lines at 0.59 μ, 0.83 μ and 1.4 μ, and by observing the position of the emission band of CO_2 at 2.7 μ. The wave-length of this band has been determined by Paschen. The position of the sodium lines was determined[3] by mounting an electric arc of cored carbons, filled with pure sodium chloride, in place of the acetylene flame and noting the circle read-

[1] G. Krüss, Kolorimetrie, last ed., also Berlin Chem. Ges., 17, p. 2732 (1884).
[2] Paschen, Wied. Ann., 51, p. 1 (1894.)
[3] Snow, PHYSICAL REVIEW, Vol. I., p. 28 (1894).

ing at which a deflection was produced by these lines. The position of the CO_2 band was similarly observed by using a Bunsen acetylene burner. The calibration curve plotted from the observed readings is given in Fig. 7. The computed circle readings for the

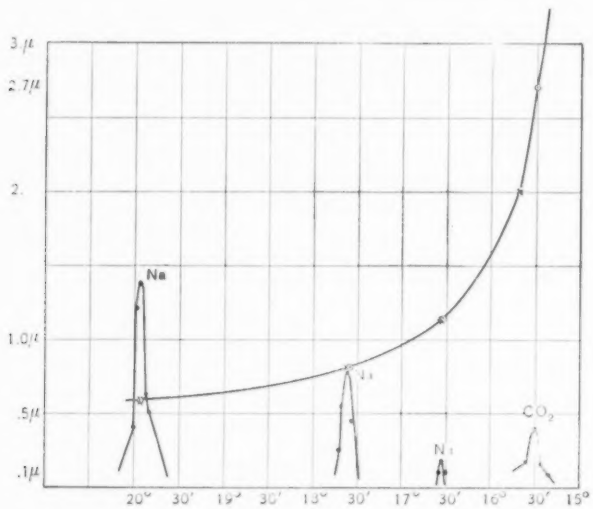

Fig. 7.

same lines—indicated on the same curve by the crosses (* *), were obtained by assuming the indices of refraction of CS_2 as determined by Rubens,[1] the prism in these computations being taken at minimum deviation for each line.

3. *Curves and Results.* — Observations were made with and without the cell of iodine solution interposed in the path of the incident light, and the ratio of the deflections gave the percentage of transmission. At first the entire spectrum to 2.7 μ was explored, using a single solution. This was found impracticable far in the infra-red on account of the absorption band of CS_2 found by Paschen[2] at 2.7 μ, the increased absorption of the glass, and the very narrow dispersion of the spectrum in this region. Between 1.8 μ and 2.7 μ a slight variation in the circle reading caused a great variation in transmission through the same solution.

[1] Rubens, Wied. Ann., 53 (1894).
[2] Paschen, Wied. Ann., p. 337 (1894).

To avoid errors in setting the collimator, from 1.8 μ to 2.7 μ, a less convenient method had to be adopted. The collimator arm was set so that a given region of the spectrum fell upon the radiometer vane, and the transmission of the entire group of solutions was found without changing the setting. This method gave consistent results. The influence of the walls of the cell and the solvent were eliminated as in the case of the spectrophotometric observations already described, by determining the transmission through the cell when filled with clear carbon bisulphide.

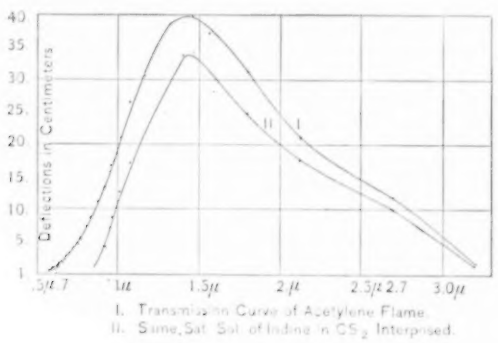

Fig. 8.

The absorption of the cell when filled with a saturated solution of iodine in CS_2 is best illustrated by the curves in Fig. 8. The ordinates are deflections in centimeters, and the abscissæ are wavelengths. Curve I. shows the deflections in various parts of the spectrum when the radiometer vane was exposed to the uninterrupted rays of the acetylene flame, while curve II. shows the corresponding deflections after the light has passed through the cell containing the iodine solution. The ratio of the two curves beyond .76 μ is about .77.

Table V. gives the percentage of radiation transmitted by the cell filled with clear CS_2, and with various concentrations of iodine ranging from 2.5 milligrams per c.c. to saturation.

The data contained in this table are shown graphically in Fig. 9, from which it will be seen that the cell containing clear CS_2 is not uniform in its transmitting power for different rays, the curve being a minimum at about 1.0 μ, and a maximum at 1.8 μ. The

TABLE V.

Transmission of Iodine in Carbon Bisulphide.

Wave-lengths.	Transmission, $I_t \div I_0$.					
Concentrations.	Cell + Clear CS_2.	2.5 mg. per c.c.	5 mg.	10 mg.	20 mg.	Saturated Solution.
.73 μ	63	2	00	00	00	00
.76	64.5	34	18	7	00	00
.78	65	43	31	18	5	00
.81	66	53	44	34	17	00
.84	65	55	50	46	35	00
.88	62	59	54	52	48	11
.92	61	—	58	54	56	32
.97	61	57	—	60	59	48
1.02	63	—	59	62	61	54
1.08	64	61	—	63	—	—
1.16	65	65	62	66	63	64.5
1.26	67	68.5	70	69	66	68
1.40	70	71.5	69	71.5	70	71
1.56	74	75	74	74	75	76
1.80	78	78.5	75	76.5	78.5	79
2.12	73	72.5	72.5	72	73.5	73.5
2.70	59	57	55	59	57.5	57.5

curves for the transmitting power of the cell when filled with the iodine solutions rise rapidly from zero in the region between 0.7 μ and 0.9 μ and join the curve for the clear CS_2 at about 1.1 μ. It ap-

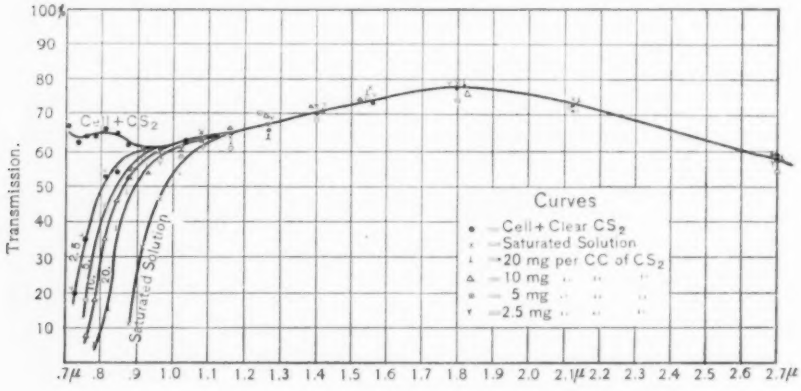

Fig. 9.

pears that beyond this point the addition of iodine to the solution has no effect whatever upon the transmitting power. This effect

will be noticed again in considering the transmission through solid films of iodine, while the absorption band is of interest in the work on anomalous dispersion.

Similar measurements of the transmission of iodine in ethyl alcohol were made, but it was found impossible to carry the observations

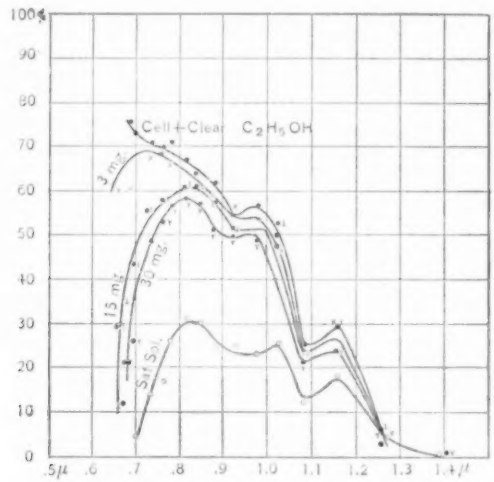

Fig. 10.

beyond 1.4 μ on account of the increasing opacity of the alcohol, the transmission of which at that wave-length was only 3 per cent.

The transmission of iodine in alcohol is shown in Fig. 10, from which it will be seen that the alcohol was by no means free from water, as is evident from the presence of the narrow absorption bands at 0.93 μ and 1.08 μ. This gives an excellent check of the spectrometer calibration for this region. Abney and Festing[1] have published photographs of the infra-red absorption spectrum of ethyl alcohol, which shows these bands. The observations of E. F. Nichols[2] also agree with the above, showing that alcohol becomes opaque at about 1.4 μ. It seems probable that the presence of these bands and the rapidly increasing opacity of the alcohol for the longer wave-lengths is due to the presence of water. Puccianti[3] has published descriptive curves for pure alcohol which show that the transparency extends beyond 1.4 μ. Table VI. gives the

[1] Abney and Festing, Phil. Trans., Vol. 172, p. 887 (1881).

[2] E. F. Nichols, PHYSICAL REVIEW, Vol. 1, p. 1.

[3] Puccianti, Nuovo Cimento, Vol. 2, p. 241 (1900).

measurements of iodine dissolved in alcohol, for solutions containing respectively 3, 15 and 30 milligrams per c.c. — also a saturated solution.

TABLE VI.

Transmission of Iodine in Ethyl Alcohol.

Wave-lengths.	Transmission, $I_t \div I_0$.			
Concentrations.	Cell + Clear C_2H_5OH.	15 mg. per c.c.	30 mg.	Saturated Solution.
.68 μ	76	40	21	00
.70	73	44	26	4
.73	73	56	49	14
.76	70	58	53	17
.78	71	59	57	26
.81	67	60	58	31
.84	64	61	57	30
.88	62	57	51	25
.92	54	51	49.5	25
.98	56	—	49	23
1.02	52.5	52	40	25.5
1.08	25	23	21.5	12.5
1.16	30	29.5	24	18
1.28	5	5	4	4
1.40	3	3	4	3

The question of the difference in absorption of new and old solutions, *i. e.*, "velocity reaction," is illustrated by the curves in Fig. 11 which show the transmission through a saturated solution while new, curve I., and after standing thirty-one days, curve II. The comparison is not quite a fair one in the regions where the energy transmitted is small, *e. g.*, beyond 1.6 μ, because for the first curve a very stiff fiber was used, while for the second curve the radiometer was almost fourteen times more sensitive. But, as a whole, they show that no chemical action occurred.

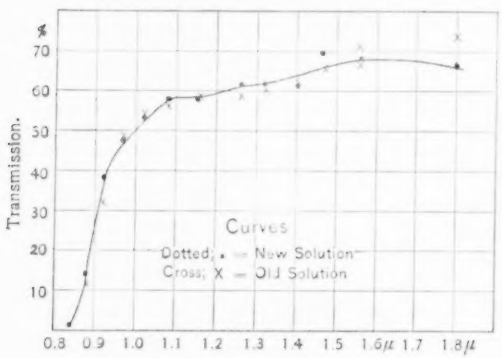

Fig. 11.

(To be concluded.)

THE EFFECT OF HIGH TEMPERATURES ON THE CHANGE OF RESISTANCE OF BISMUTH IN A MAGNETIC FIELD.

By Frank B. Jewett.

IN a series of experiments carried on at Ryerson Physical Laboratory, University of Chicago, during the winter of 1899–1900, some interesting results were obtained regarding the effect of high temperatures on the change of resistance of bismuth wire in a magnetic field. The experiments were originally undertaken simply to determine the allowable temperature variations in the ordinary form of commercial spiral, as used in measuring field strengths. As the results soon showed, however, that at the higher temperatures the change of resistance curve varied greatly from its mean temperature form, the experiments were carried on much beyond the originally set limits. A few of the results, together with a short description of the method employed in forming the spirals, are appended in the following article.

The commercial spiral as prepared by Hartman & Braun, consists simply of a flat, non-inductive coil of comparatively fine wire having a resistance of from 12 to 20 ohms. The manner of making the wire would seem to point to a crystallographic formation such that any direction through the coil is one of mean resistance; this was the assumption though no microscopic examination of a wire section was made.

At the time of the experiments the impossibility of procuring bismuth wire made the employment of a quick and simple process for its manufacture necessary. After a number of trials the following scheme was adopted as giving more satisfactory results than the ordinary mode of casting in capillary tubes. Two long pieces of cast iron were first planed smooth and fitted with machine screws for clamping them firmly together; shallow, slightly trapezoidal grooves were then planed in one of the pieces and a reservoir cut

in one end (Fig. 1); the grooves were highly polished in order to facilitate the removal of the castings. These latter were formed by standing the mould, heated almost to redness, upon an iron plate and pouring molten bismuth into the upper or reservoir end. Since bismuth is malleable at about 200° C. the cap plate was taken off the mould while still quite hot and the castings removed. The wires thus formed, while of the desired length, were neither of the right shape nor cross section to be easily worked; to reduce the amount of metal, the strips were clamped between pieces of

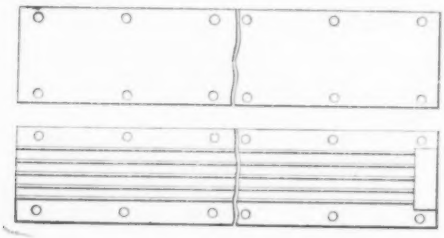

Fig. 1.

heavy sheet brass and the whole filed down the requisite amount. This filing breaks up the crystalline continuity and renders the metal extremely friable; recrystallization is accomplished by transferring the now more or less square filament to a metal plate whose temperature is slightly above the melting point of bismuth. This process serves a double end, for not only does it recrystallize the metal, but at the same time the surface tension causes the wire to assume a form of almost circular cross section. Care must be exercised lest the plate be too hot, in which instance the surface tension causes the wire to break and collect in globules. With the aid of a hot plate the wire formed as above can be readily worked into any desired shape. The spiral once formed the only remaining difficulty is in fastening on the terminal wires — for low temperatures this can be readily accomplished by the use of ordinary soft solder, but as such a joint is in reality simply a piece of fusible metal, other methods must be employed when the temperature is to be above 90° C. After many fruitless attempts pure bismuth was found to answer better than any other solder, although its application is somewhat difficult. To facilitate handling and at the same time protect the

spiral from chance injury it was enclosed in a shallow fiber capsule with screw top.

In order to obtain consistent results, it is of prime importance that the bismuth employed be as pure as possible, slight admixtures of foreign metals causing great variations in behavior under identical conditions. In the following work the castings were made from metal electrolytically deposited from an acid nitrate solution with a rod of Kohlbaum's C. P. for an anode. The variations in the behavior of specimens *A* and *B* (Tables I. and II.) are probably due to the fact that the wires of which the two spirals were constructed had considerably different diameters, and as is well known, the size of the crystals vary with the dimensions of the casting, when the latter is not made under pressure.

For keeping the spiral at any desired temperature, a bath of heavy mineral oil was used; the box containing the oil was of brass, furnished with insets at the sides to permit of the close adjustment of the pole pieces. The heating was accomplished by means of Bunsen burners and fairly constant and uniform temperatures were maintained by means of an electrically driven propeller. The magnet used was one designed to give a uniform field of 35,000 C.G.S. units over a considerable area for pole pieces 3 mm. apart.

Discussion of the Results. — In making the determinations the process was simply to bring the spiral to the desired temperature, and after constant conditions had been attained, to measure the resistance in fields of various strengths. A condensed outline of the results is given in Tables I. and II. and the corresponding curves are plotted in Figs. 2 and 3 — Table I. and Fig. 2 refer to specimen *A* — Table II. and Fig. 3 to specimen *B*. In plotting the curves, abscissæ were taken to represent field strengths in C.G.S. units and ordinates to represent percentage changes of resistance — $\frac{R - Ro}{Ro}$, where R is the resistance of the spiral at any temperature in field H and Ro is the resistance at the same temperature outside the magnetic field.

Upon examining the plates it will be noticed that in every case, with the possible exception of the one for 24°, the curves seem to

consist of two straight lines representing regions of uniform variation, connected by a more or less extended curve denoting a region of non-uniform variation — in each case also the percentage change is greater in the second half of the curve. As the temperature of

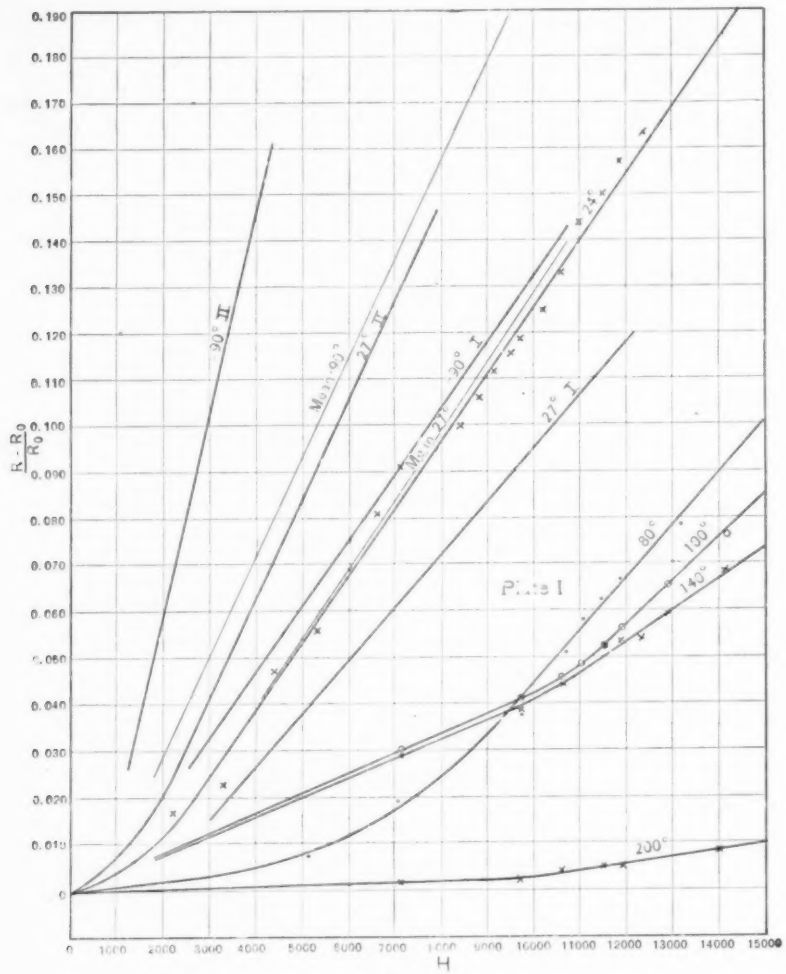

Fig. 2.

the spiral is raised this variable portion seems to travel toward the region of denser magnetic flux.

Even more striking is the apparent existence of fairly well defined temperatures of subsidiary minimum and maximum variation in the

region below $H = 10{,}000$. For spiral B the number of readings was too small to give anything but a general idea as to the location of these points; in the case of A, however, if the readings for vari-

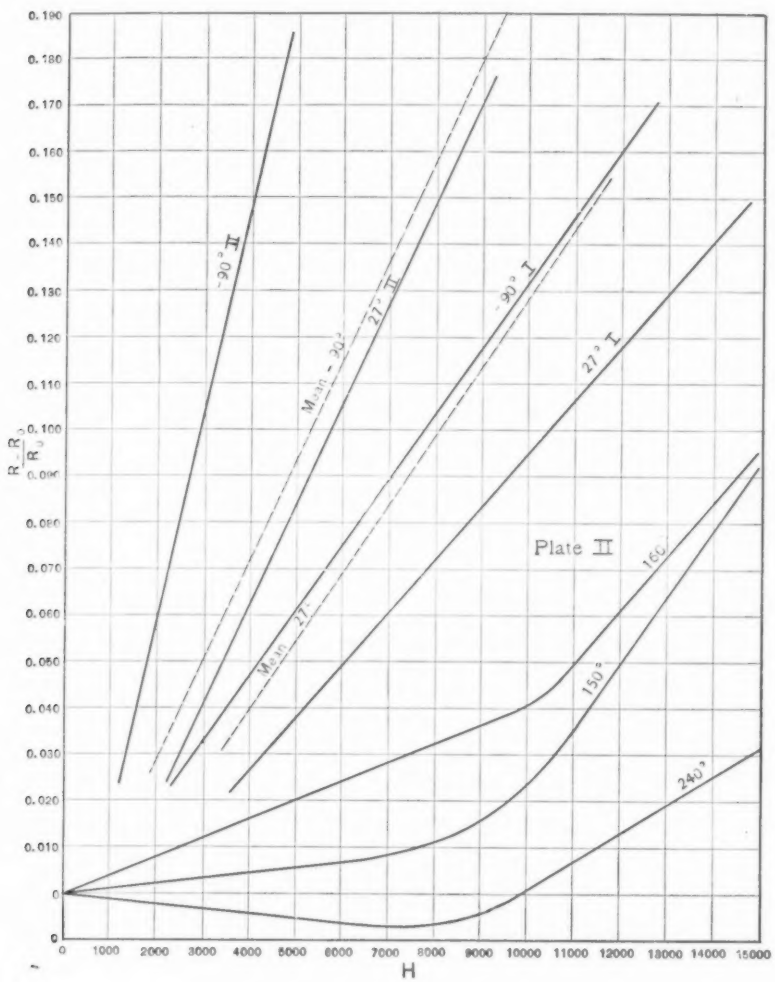

Fig. 3.

ous values of H are plotted with $\frac{R - Ro}{Ro}$ as ordinates and temperatures as abscissæ (Fig. 4), it is seen that the point of minimum variation is in the neighborhood of 80°, while the succeeding maxi-

mum occurs somewhere between 100° and 115°. Beyond this point further increase in temperature causes a continuous diminution in the percentage change of R with respect to H. It is also evident that the greatest variation occurs for $H = 6{,}000$ and that the minimum disappears at about $H = 9{,}600$.

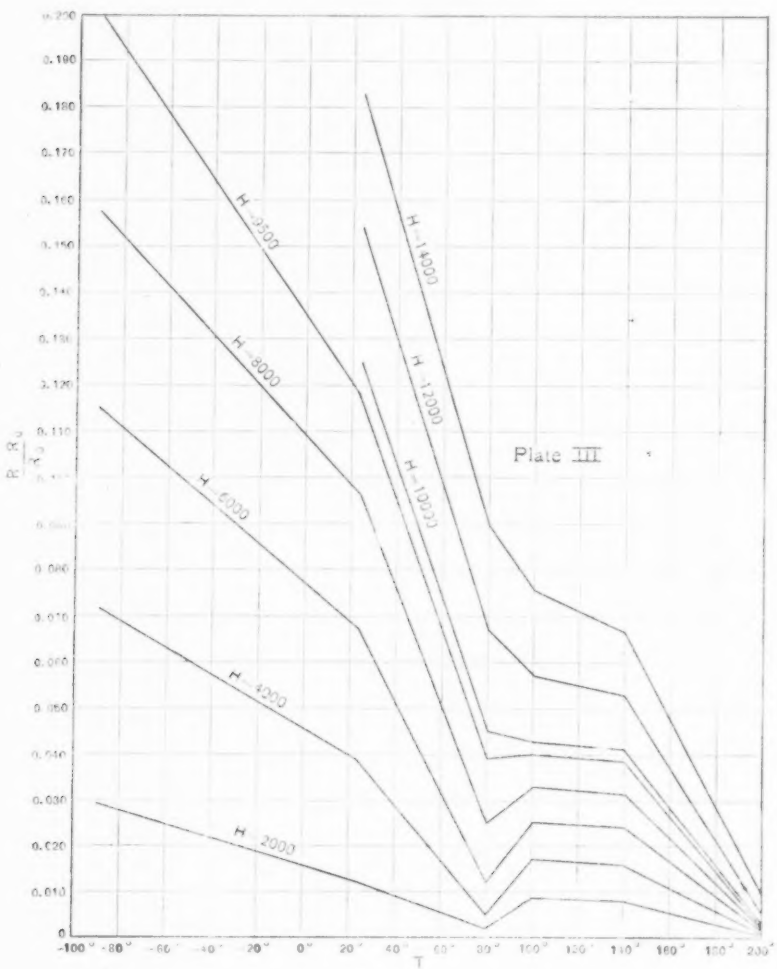

Fig. 4.

While not plotted the corresponding curves for specimen B would apparently be quite similar — so far at least as regards the point

of maximum field influence; the point of minimum disappearance for this specimen is somewhere near $H = 18{,}000$.

In both Figs. 3 and 4 are plotted curves showing the variation of resistance for 27° and — 90°; these curves are from a few readings taken by Dr. E. Van Everdingen, Jr.,[1] while experimenting on the Hall effect in crystalline bismuth plates at very low temperatures. The curves marked I. were from readings taken with the direction of maximum resistance in the rod coinciding with the lines of force. Curves II. have this direction perpendicular to the lines. In both plates the mean of the two curves are shown by the dashed lines and the proximity of the mean for 27° to the curve for 24° would seem to indicate that the previously stated assumption regarding the direction of mean resistance in the spiral was justifiable. The values of $\frac{R - Ro}{Ro}$ for — 90° in Fig. 4 are those of the mean curve for that temperature.

While the curve for spiral B at 240° shows a negative value for $\frac{R - Ro}{Ro}$ between $H = 0$ and $H = 10{,}000$, it is doubtful if much reliance can be placed on it, as two or three sets of readings on A at neighboring temperatures above and below this point, showed that at about 245° the metal loses entirely the property of change of resistance in a magnetic field. This is what would be expected since bismuth loses its crystalline structure at about 245–250°. (In this connection it is interesting to note that with thin plates of non-crystalline bismuth, formed by means of the cathode stream, no evidence of any magnetic effect on the resistance was observable even at field strengths as high as 27,000.)

It is to be regretted that a larger number of readings at shorter temperature intervals was not made, but as at the time none of the results were plotted, the peculiar inversion effect was inadvertently overlooked. In case the experiments were to be repeated it would seem advisable to discard the cast spiral form entirely and use slender rods cut from electrolytically deposited plates, as was done by Dr. Van Everdingen; this would permit of determinations being made for both positions of the axis of maximum resistance.

[1] E. Van Everdingen, Jr., Verslagen van de Afdeeling Watnurkunde der Kon. Akademie van Wetenschappen te Amsterdam, Oct. 28 and Dec. 30, 1899.

TABLE I.

Temp.	H	R	$\frac{R-Ro}{Ro}$	Temp.	H	R	$\frac{R-Ro}{Ro}$
24.0	0	1.322	0	100	0	1.358	0
24.0	2,200	1.345	0.017	100	7,100	1.399	0.030
24.0	3,300	1.353	0.023	100	9,700	1.414	0.041
24.0	4,400	1.385	0.047	100	10,600	1.420	0.045
24.0	5,300	1.397	0.056	100	11,000	1.424	0.048
23.5	6,000	1.414	0.069	100	11,500	1.429	0.052
23.5	6,600	1.430	0.081	100	11,900	1.434	0.056
24.0	7,100	1.443	0.091				
24.0	8,400	1.454	0.100	140	0	1.383	0
24.0	8,800	1.463	0.106	140	7,100	1.423	0.029
24.0	9,100	1.469	0.112	139.5	9,700	1.436	0.038
24.0	9,500	1.476	0.116	140	10,600	1.445	0.044
24.0	9,700	1.480	0.119	140	11,000	1.452	0.049
24.0	10,200	1.488	0.125	140	11,500	1.455	0.052
24 0	10,600	1.498	0.133	140.5	11,900	1.456	0.053
24.0	11,000	1.512	0.144	139.5	12,300	1.458	0.054
24.0	11,500	1.521	0.150				
24.0	11,900	1.530	0.157	200	0	1.353	0
24.0	12,400	1.537	0.163	200	7,100	1.356	0.0022
				199.5	9,700	1.356	0.0022
79.5	0	1.334	0	201	10,600	1.358	0.0037
80.5	7,100	1.360	0.019	199.5	11,000	1.360	0.0052
80.0	9,700	1.386	0.038	200	11,500	1.360	0.0052
80.0	10,600	1.401	0.050	200	11,900	1.360	0.0052
80.0	11,000	1.410	0.057				
79.5	11,500	1.417	0.062				
79.5	11,900	1.422	0.066				

TABLE II.

Temp	H	R	$\frac{R-Ro}{Ro}$	Temp.	H	R	$\frac{R-Ro}{Ro}$
148	0	1.288	0	240	0	1.227	0
148	8,200	1.303	0.012	240.5	7,100	1.218	−0.007
147	9,700	1.320	0.025	240	9,700	1.225	−0.001
149.5	10,600	1.320	0.025	239.5	10,600	1.250	0.019
149	11,300	1.340	0.040	239	11,500	1.255	0.022
149.5	12,300	1.400	0.087(?)	241	11,500	1.250	0.019
				241	11,900	1.240	0.012
160	0	1.297	0				
160	7,100	1.335	0.029				
160	9,700	1.348	0.039				
159	10,600	1.355	0.044				
158.5	11,000	1.364	0.051				
160	11,500	1.372	0.057				
160	11,900	1.373	0.058				

In conclusion I wish to express my appreciation of the interest shown throughout the work by Professors Michelson and Stratton, and to thank Professor Stratton for many suggestions given. My thanks are also due to Dr. Earhart for help rendered in the preliminary readings.

BOSTON, MASS.,
October 23, 1902.

NOTE ON MAGNETOSTRICTION IN BISMUTH.

By Edmond van Aubel.

MR. A. P. WILLS published in the issue of the Physical Review for July, 1902, an interesting memoir on magnetostriction in bismuth. Using intense magnetic fields up to 3200 C.G.S. units, this physicist undertook to determine whether bismuth undergoes elongation when submitted to the action of magnetism. Such an elongation was found by Shelford Bidwell, in 1888, and was considered as very perceptible, even with the magnetic field of 470 C.G.S.units.

It seems well to call attention to several articles published previously on the same subject, and which have escaped the notice of the American physicist. Taking them altogether, we can draw from them the same conclusion as that reached in the experiments of Mr. Wills.

Tyndall[1] was probably the first to examine the question, but he observed no variation in length. Later, G. P. Grimaldi[2] undertook to find out whether the great influence exercised by magnetism on the electric resistance and on the thermoelectric power of bismuth could be explained by certain deformations which this metal underwent in the magnetic field. Even with a very sensitive apparatus he was unable to find any variation of length in bars of bismuth about 30 to 40 cm. long.

In 1892 I also examined the influence of magnetization on the length of a bar of bismuth,[3] using Fizeau's method of interference fringes, and a bar of bismuth 31 cm. long. This was made of the absolutely pure metal that had been used by Classen for the deter-

[1] Tyndall: On Some Mechanical Effects of Magnetization, published in his Researches on Diamagnetism and Magnetocrystallic Action, London, 1870.

[2] Nuovo Cimento, Third Series, Vol. 23, p. 211, 1888. Journal de Physique, Second Series, Vol. VIII., p. 552, 1889.

[3] Journal de Physique, 3d Series, Vol. 1, page 424, 1892. Gustav Wiedemann, Die Lehre von der Elektricität, second edition, vol. 3, page 1023, 1895.

mination of atomic weight, and which I had used in my researches on electric resistance. Nevertheless no elongation could be found. In the report of the meeting of the Royal Society of Edinburgh,[1] May 16, 1899, we find the following statement: "Dr. C. G. Knott gave a short note on Magnetic Strains in Bismuth. A slight indication has been obtained that there was a change of form in bismuth when strongly magnetized, but the indication was so slight that it was more prudent meanwhile to reserve judgment." Several days later Shelford Bidwell called attention in the same review[2] to the fact that he had observed, in 1888 (Philosophical Transactions), an elongation in a bar of bismuth amounting to 1.5 ten-millionths of the length for a magnetic field of 840 C.G.S. units. He has, since that time, repeated the same experiment with another sample of bismuth furnished by Messrs. Johnson and Matthey, but, although the magnetic field was now carried up to about 1500 units, he could not even then observe the least indication of any change in the length.[3] Nevertheless an elongation ten times less than that previously observed could have been noticed. So Shelford Bidwell adds: "After this experiment I should hesitate to attach importance to any such observations, unless the bismuth employed had been proved by analysis to be free from traces of magnetizable metals."

This interesting article is followed by several lines by C. G. Knott, who recognizes the necessity of working with the pure metal, but declares that he has not paid especial attention to this point in his experiments. In a letter which he afterwards did me the honor to send to me, the same physicist wrote that he considered the bismuth with which he had worked as certainly impure, although the metal had been as pure as possible. The effect observed was, moreover, very weak and doubtful.

In 1899,[4] *Nature* published a note by me on the same subject, in which note I called attention to the fact that I had obtained similar results with a piece of bismuth whose purity was beyond doubt, and by the use of a very sensitive method.

[1] Nature, London, June 22, 1899, page 191.

[2] Nature, London, July 6, 1899, page 222.

[3] "There was never the smallest indication of any magnetic change of length."

[4] Nature, London, August 17, 1899, page 374.

This bibliography shows that all the experiments made up to this time agree to establish the fact that a bar of pure bismuth does not change in length in a magnetic field.

Mr. Will's experiments, also performed apparently with the pure metal, and in powerful magnetic fields reaching up to 3200 C.G.S. units, give additional confirmation of the previous results.

UNIVERSITY OF GHENT,
August, 1902.

NEW BOOKS.

The Electric Arc. By HERTHA AYRTON. Pp. xxv + 479. New York, Van Nostrand; London, The Electrician Publishing Co., 1902.

At the Electrical Congress in Chicago in 1893 Professor Ayrton read a paper on the electric arc, the manuscript of which was destroyed by fire before publication. Those who had the pleasure of listening to his paper will recognize in Mrs. Ayrton's volume the restatement in fuller form of its salient features, together with a wealth of new experimental material of her own. The book is in form and character indeed a scientific memoir in which the results of the author's own investigations are given in great detail. This method of publishing the results of an extended investigation, while unusual, possesses many advantages. It is possible in the first place, as Mrs. Ayrton has done, to give nearly a hundred pages to a history of the scientific literature and to describe in an adequate manner the work of one's contemporaries, instead of merely alluding to them in footnotes, which is all that is possible to the author who publishes his results in the scientific journals. In this way only can the bearing of one's work to that which has gone before be properly brought out and the real nature of the advance which has been made be clearly indicated.

The difference between Mrs. Ayrton's volume and the ordinary scientific compilation will be apparent from the statement that with the exception of the introductory chapters on the appearance, and history of the arc, and three brief appendices, there is no chapter in which her own work does not occur as the central feature around which the investigations of others are grouped. The inevitable result is, of course, a certain incompleteness, due to the fact that many topics which would naturally enter into a treatise on the electric arc are omitted altogether. Of arc lamps as such, for example, nothing is said. The volume deals solely with the physics of the arc and almost exclusively with the physics of the direct-current arc, since it is with this form chiefly that Mrs. Ayrton's own experiments deal. Of the spectrum of the arc, which in itself would afford material for a second memoir not less extensive than that which Mrs. Ayrton has written, nothing is said, and there are a dozen other topics which one might reasonably look for concerning which she has remained silent. The ten chapters which form the substance of the vol-

ume, deal with the following topics: The phenomena connected with the striking of the arc and with sudden variations of current; the steady potential difference between the carbons when the length of the arc is fixed and the current varied, and when the current is fixed and the length of the arc is varied; the area of the crater; the depth of the crater; the relations between the diameters of the carbon and the potential difference between them; the apparent resistance of arc with constant current; the relation between the current and length of arc for constant potential difference; the relations between the power and length of arc for constant currents and between power and current for constant lengths of arc; the relations between the E.M.F., the resistance of the outside circuit; the length of the arc and the current; the ratio of the power expended in the silent arc to the power expended by the generator; phenomena of hissing arcs; the light emitted by the arc under various conditions: its luminous efficiency and the conditions of maximum luminous efficiency; the mechanism of the arc; its true resistance; the question of a back E.M.F.

The most striking and perhaps the most important contributions to our knowledge in this work are those which relate to hissing arcs and to the effects produced by what Mrs. Ayrton calls *arc vapor* and *arc mist*. While the really important portions of the memoir might have been condensed into a paper of 100 or perhaps less pages, the service which Mrs. Ayrton has done to the science of physics in presenting the results of her investigation in this fuller form is certainly greater than though she had contented herself with the usual brief and cursory method of publication. The growth of the literature of science has in recent years been such as to make it almost impossible for even the most indefatigable of readers to keep in familiar touch even with those topics in which he is chiefly interested. Any one, therefore, who having completed an investigation will take the trouble to present in connection with his own work a fair and lucid description of what has been done before in the same field, even though this may necessitate the expansion of the memoir to several hundred pages is, like the present author, deserving of special recognition and of the thanks of all colaborers.

E. L. N.

THE PHYSICAL REVIEW beginning with Vol. XVI. (January–June, 1903) will be conducted with the co-operation of the AMERICAN PHYSICAL SOCIETY. The separate publication of the BULLETIN of the Society has been discontinued and its Proceedings are hereafter to be published regularly in the REVIEW.

The Proceedings of the Washington meeting of the Physical Society (December, 1902) will appear in the March number of the REVIEW.